DETOXIFICATION OF CHLORINATED ORGANIC COMPOUNDS USING FLUIDIC MICROREACTOR WITH GAS CHROMATOGRAPHY/MASS SPECTROMETRY

BY

ABDULELAH AHMED ALI THABET

A Thesis Presented to the
DEANSHIP OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMISTRY

May, 2013

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN- 31261, SAUDI ARABIA

DEANSHIP OF GRADUATE STUDIES

This thesis, written by **Abdulelah Ahmed Ali Thabet** under the direction his thesis advisor and approved by his thesis committee, has been presented and accepted by the Dean of Graduate Studies, in partial fulfillment of the requirements for the degree of **MASTER OF SCIENCE IN CHEMISTRY.**

Dr. Basheer Chanbasha
(Advisor)

Dr. Mohammed Al-Daous
(Member)

Dr. Abdullah J. Al-Hamdan
Department Chairman

Dr. Than Htun Maung
(Member)

Dr. Salam A. Zummo
Dean of Graduate Studies

27/5/13
Date

DEDICATED

TO

My Beloved Parents for their Prayers and My Brothers, Sisters, children & Wife for their Care & Support

ACKNOWLEDGMENTS

All praise and glory goes to Almighty Allah for granting me the guidance, patience, health, and ability to successfully accomplish this work.

I would like to express my deep appreciation to my thesis advisor Dr. Basheer Chanbasha , for his constant help, guidance, encouragement and invaluable support. Appreciation is also to my thesis committee members Dr. Mohammed Al-Daous, and Dr. Than Htun Maung for their cooperation, comments and support.

I would like to thank the Deanship of Scientific Research at King Fahd University of Petroleum and Minerals for funding this research (project # SB111009). I also would like to thank Sana'a University which gives me the opportunity for completing my MSc degree in KFUPM.

I would like also to thank the chemistry department, beginning with the chairman Dr. Abdullah J. Al-Hamdan, the graduate advisor Professor. El-Ali, all faculty members, the technical staff and my colleagues in the department for their direct or indirect help.

Also, thanks for all Yemeni colleagues in KFUPM who help and support me during a very difficult time in my live when I was very sick, especially Mr. Abdullah Alswat.

Finally, I would like to thank my Parents, Brothers, Sisters, children & Wife who always Support me with their love, patience, encouragement and constant prayers.

TABLE OF CONTENTS

ACKNOWLEDGMENTS ..... **V**

TABLE OF CONTENTS ..... **VI**

LIST OF TABLES ..... **VIII**

LIST OF FIGURES ..... **X**

LIST OF ABBREVIATIONS ..... **XV**

ABSTRACT ..... **XVII**

CHAPTER 1 INTRODUCTION **1**

1.1 Chlorinated organic compounds (COCs) **1**

1.1.1 Description, uses, classification, impacts and examples of COCs **1**

1.2 Catalytic hydrodechlorination (HDC) of COCs **4**

1.2.1 Description, Advantages, Catalysts, Microreactor **4**

1.3 OBJECTIVES **8**

1.4 PROBLEM STATEMENT **8**

CHAPTER 2 LITERATURE REVIE **10**

2.1 Section Chlorinated organic compounds (COCs) **10**

2.2 Detoxification methods of COCs **11**

2.3 Catalytic hydrodechlorination (HDC) of COCs **12**

2.4 Detoxification of CBs and CPs over supported catalysts **14**

2.5 HDC reaction in a capillary-microreactor **15**

CHAPTER 3 RESEARCH METHODOLOGY **17**

3.1 Materials **17**

3.2 Synthesis of RHA-Pt and RHA-Ti Supported Catalysts 18
3.3 Catalysts Characterization 19
3.3.1 FT-IR spectral analysis 19
3.3.2 N_2 adsorption–desorption analysis 23
3.3.3 SEM and EDX analyses 25
3.4 Catalytic hydrodechlorination (HDC) by conventional method 32
3.5 HDC reaction in a capillary-microreactor 34
3.6 Commonly found COCs in water: Target compounds 37
3.7 Instrumental Analysis Condition 39
CHAPTER 4 RESULTS & DISCUSSIONS 41
4.1 PART 1: Detoxification of COCs using conventional method 41
4.2 PART 2: Detoxification of COCs using capillary microreactor 57
4.2.1 Optimization of capillary microreactor method for the HDC reaction 57
4.2.2 Applied potential 57
4.2.3 Effect of Reaction time 63
4.2.4 Length of the capillary-microreactor 67
4.2.5 Reaction pH 71
4.2.6 Quantitative determination of Detoxification of COCs using the microreactor with (GC-MS) ... 75
4.3 Mechanism of the dechlorination of CBs and CPs 81
CHAPTER 5 CONCLUSION & RECOMMENDATION 84
5.1 CONCLUSION 84
5.2 RECOMMENDATIONS 85
REFERENCES 86
VITAE 90

LIST OF TABLES

Table 3-1 The nitrogen adsorption–desorption analysis parameters of materials 23

Table 3-2 Gas Chromatographic conditions for the determination of COCs 40

Table 4-1The Effect of different reaction times on the conversion ratio by the conventional method by using phosphate buffer of pH 2 and RHA-Pt and RHA-Ti catalysts..... 42

Table 4-2 The Effect of different reaction times on the conversion ratio by the conventional method by using phosphate buffer of pH 7 and RHA-Pt and RHA-Ti catalysts..... 43

Table 4-3 The Effect of different reaction times on the conversion ratio by the conventional method by using phosphate buffer of pH 10 and RHA-Pt and RHA-Ti catalyst 44

Table 4-4 Effect of different applied potentials on the conversion ratio in the capillary-microreactor (at reaction time 20min and pH10 by using RHA-Pt 59

Table 4-5 Effect of different applied potentials on the conversion ratio in the capillary-microreactor (at reaction time 10 and pH 10 by using RHA-Ti)..... 60

Table 4-6 Effect of different reaction times on the conversion ratio in the capillary-microreactor of 21cm Length by applied potential 3kV 64

Table 4-7 Effect of Length of the capillary microreactor on the conversion ratio of CBs and CPs 68

Table 4-8 Effect of reaction pH on the conversion ratio of COCs in the capillary-microreactor (at 20min and applied potential 3kV) 72
Table 4-9 Conversion ratio of CBs and CPs by the capillary-microreactor and the conventional method 76
Table 4-10 Compound name, retention time and peak number of target compounds in the GC-MS chromatogram 80

LIST OF FIGURES

Figure 2-1 Schematics of (a) the glass capillary microreactor for transfer hydrogenolysis reaction (b) Conventional experimental set up for hydrodechlorination reaction with external supplied hydrogen gas source 16

Figure 3-1.The FT-IR spectra of RHA silica and metal modified silica by loading10% (Ti and Pt) (a) RHA-SiO_2, (b) RHA-Ti, (c) RHA- Pt. 20

Figure 3-2 FT-IR spectra of (a) TiO_2, (b) RHA-Ti (c) RHA-SiO_2 21

Figure 3-3 FT-IR spectra of (a) $PtCl_2$, (b) RHA-SiO_2, (c) RHA-Pt 22

Figure 3-4 The nitrogen adsorption–desorption analysis of materials (a) RHA-silica(b) RHA-Pt (c) RHA-Ti 24

Figure 3-5 The FESEM image of (a) RHA- silica (b) is the SEM of the area of the RHA-silica sample from which EDX is measured 26

Figure 3-6 EDX spectrum of RHA- silica (a): Inset is th percentages of the RHA-silica component in the sample 27

Figure 3-7 The FESEM image of RHA-Ti (a) 500nm and (b) 1µm 28

Figure 3-8 EDX spectrum of RHA-Ti. Inset is th percentages of the RHA-Ti component in the sample 29

Figure 3-9 The FESEM image of RHA-Pt (a) 500nm and (b) 2µm 30

Figure 3-10 EDX spectrum of RHA-Pt. Inset is th percentages of the RHA-Pt component in the sample 31

Figure 3-11 Schematics of the conventional method experimental setup for transfer hydrogeniysis reaction with external supplemented hydrogen gas source (H_2 in balloon) 33

Figure 3-12 Glass capillary microreactores various lengths (7cm, 14cm, 21cm) which designed and used for the HDC reaction 35

Figure 3-13 Experimental set-up of the capillary-microreactor system used for the detoxification of chlorinated organic compounds..... 36

Figure 3-14 chemical structures of target chlorinated organic compounds COCs 38

Figure 4-1 The Effect of reaction pH on the conversion ratio of chlorobenzenes (CBs) by the conventional method (after 2HR) by using (a) RHA-Pt and (b) RHA-Ti 45

Figure 4-2 The Effect of reaction pH on the conversion ratio of Chlorophenols (CPs) by the conventional method (after 2HR) by using (a) RHA-Pt and (b) RHA-Ti 46

Figure 4-3 The Effect of reaction pH on the conversion ratio of chlorobenzenes (CBs) by the conventional method (after 16HR) by using (a) RHA-Pt and (b) RHA-Ti 47

Figure 4-4 The Effect of reaction pH on the conversion ratio of Chlorophenols (CPs) by the conventional method (after 16HR) by using (a) RHA-Pt and (b) RHA-Ti 48

Figure 4-5 The Effect of reaction pH on the conversion ratio of chlorobenzenes (CBs) by the conventional method (after 24HR) by using (a) RHA-Pt and (b) RHA-Ti 49

Figure 4-6 The Effect of reaction pH on the conversion ratio of Chlorophenols (CPs) by the conventional method (after 24HR) by using (a) RHA-Pt and (b) RHA-Ti 50

Figure 4-7 The Effect of different reaction time on the conversion ratio of chlorobenzenes (CBs) by the conventional method at pH 2 by using (a) RHA-Pt and (b) RHA-Ti..... 51

Figure 4-8 The Effect of different reaction time on the conversion ratio of Chlorophenols (CPs) by the conventional method at pH 2 by using (a) RHA-Pt and (b) RHA-Ti 52
Figure 4-9 The Effect of different reaction time on the conversion ratio of chlorobenzenes (CBs) by the conventional method at pH 7 by using (a) RHA-Pt and (b) RHA-Ti..... 53
Figure 4-10 The Effect of different reaction time on the conversion ratio of Chlorophenols (CPs) by the conventional method at pH 7 by using (a) RHA-Pt and (b) RHA-Ti 54
Figure 4-11 The Effect of different reaction time on the conversion ratio of chlorobenzenes (CBs) by the conventional method at pH 10 by using (a) RHA-Pt and (b) RHA-Ti 55
Figure 4-12 The Effect of different reaction time on the conversion ratio of Chlorophenols (CPs) by the conventional method at pH 10 by using (a) RHA-Pt and (b) RHA-Ti 56
Figure 4-13 Effect of different applied potentials on the conversion ratio of chlorobenzenes (CBs) in the capillary-microreactor (at reaction time 20min and pH 10 by using (a) RHA-Pt and (b) RHA-Ti..... 61
Figure 4-14 Effect of different applied potentials on the conversion ratio of Chlorophenols (CPs) in the capillary-microreactor (at reaction time 20min and pH 10 by using (a) RHA-Pt and (b) RHA-Ti..... 62
Figure 4-15 Effect of different reaction times on the conversion ratio of chlorobenzenes (CBs) in the capillary-microreactor of 21cm Length, applied potential 3kV (a) using pH 7 and RHA-Pt catalyst (b) using pH 10 and RHA-Ti catalyst 65

Figure 4-16 Effect of different reaction times on the conversion ratio of Chlorophenols (CPs) in the capillary-microreactor of 21cm Length, applied potential 3kV (a) using pH 7 and RHA-Pt catalyst (b) using pH 10 and RHA-Ti catalyst 66
Figure 4-17 Effect of Length of the capillary microreactor on the conversion ratio of CBs and 69
Figure 4-18 Effect of Length of the capillary microreactor on the conversion ratio of CPs 70
Figure 4-19 Effect of reaction pH on the conversion ratio of chlorobenzenes (CBs) in the capillary-microreactor (at 20min and applied potential (3kV) by using (a) RHA-Pt and (b) RHA-Ti 73
Figure 4-20 Effect of reaction pH on the conversion ratio of Chlorophenols (CPs) in the capillary-microreactor (at 20min and applied potential (3kV) by using (a) RHA-Pt and (b) RHA-Ti 74
Figure 4-21 GC-MS chromatogram of CBs and CPs using conventional method , the control 100 ppm before a reaction occurs (Top), after 2 HR (middle) and after 16 HR (bottom). Peaks: 1 (2-chloroPhenol), 2 (1,4-dichlorobenzene), 3 (1,2-dichlorobenzene), 4 (1,3-dichlorobenzene), 5 (2,4-dichloroPhenol), 6 (1,2,4-trichlorobenzene), 7 (2,4,6-trichlorophenol), 8 (2,4,5-trichlorophenol), 9 (2,3,4,6-trichlorophenol), 10 (2,3,5,6-trichlorophenol), 11 (hexachloropenzene), 12 (pentachlorophenol)..... 77
Figure 4-22 GC-MS chromatogram of CBs and CPs using the glass capillary-microreactor, the control 100ppm before a reaction occurs (Top), after 10min (middle) and after 20min (Bottom).). Peaks: 1 (2-chloroPhenol), 2 (1,4-dichlorobenzene), 3 (1,2-dichlorobenzene), 4 (1,3-dichlorobenzene), 5 (2,4-dichloroPhenol), 6 (1,2,4-

trichlorobenzene), 7 (2,4,6-trichlorophenol), 8 (2,4,5-trichlorophenol), 9 (2,3,4,6-trichlorophenol), 10 (2,3,5,6-trichlorophenol), 11 (hexachloropenzene), 12 (pentachlorophenol) 78

Figure 4-23 GC-MS chromatogram of CBs and CPs, the control 100ppm (Top), a glass capillary-microreactor after 20min (Bottom) in comparison with conventional method after 16HR (middle)). Peaks: 1 (2-chloroPhenol), 2 (1,4-dichlorobenzene), 3 (1,2-dichlorobenzene), 4 (1,3-dichlorobenzene), 5 (2,4-dichloroPhenol), 6 (1,2,4-trichlorobenzene), 7 (2,4,6-trichlorophenol), 8 (2,4,5-trichlorophenol), 9 (2,3,4,6-trichlorophenol), 10 (2,3,5,6-trichlorophenol), 11 (hexachloropenzene), 12 (pentachlorophenol) 79

Figure 4-24 The proposed degradation pathway of CBs with RHA-Ti and RHA-Pt by using capillary-microreactor 82

Figure 4-25 The proposed degradation pathway of Cps with RHA-Ti and RHA-Pt by using capillary-microreacto 83

LIST OF ABBREVIATIONS

1,2-DCB	:	1,2- DichloroBenzene
1,3-DCB	:	1,3-DichloroBenzene
1,4-DCB	:	1,4- DichloroBenzene
1,2,4-DCB	:	1,2,4-TriChloroBenzene,
HCB	:	1,2,3,4,5,6-HexaChloroBenzene.
COCs	:	Chlorinated Organic Compounds
CACs	:	Chlorinated Aromatic Aompounds
CBs	:	Chlorinated Benzenes
CPs	:	Chlorinated Phenols
HDC	:	Catalytic Hydrodechlorination
GC-MS	:	Gas Chromatography Mass Spectrometer
HCBs	:	Hexachlorobenzene
PCBs	:	Polychlorinated biphenyls
ppm	:	Parts per million (10^{-6})
USEPA	:	United States Environmental Protection Agency
μL	:	Micro liter

IARC	:	International Agency of Research on Cancer
2CP	:	2-chlorophenol
2,4-DCP	:	2,4-Dichlorophenol
2,4,5-TCP	:	2,4,5-TrichloroPhenol
2,4,6-TCP	:	2,4,6-Trichlorophenol|
2,3,4,6-TeCP	:	2,3,4,6 Tetrachlorophenol
2,3,5,6-TeCP	:	2,3,5,6-tetrachloroPhenol
PCP	:	PentachloroPhenol
RHA	:	Rice Husk Ash
RHA-Pt	:	Rice Husk Ash- Platinum
RHA-TiO_2	:	Rice Husk Ash- Titania
RHA-SiO_2	:	Rice Husk Ash- Silica
EDX	:	Energy Dispersive Spectrometry
FESEM	:	Field-Emission Scanning Electron Microscope
FT-IR	:	Fourier Transform Infrared

ABSTRACT

Full Name : Abdulelah Ahmed Ali Thabet

Thesis Title : Detoxification of Chlorinated Organic Compounds using Fluidic Microreactor with Gas Chromatography/Mass Spectrometry

Major Field : Chemistry

Date of Degree : May 2013

Chlorinated organic pollutants are persistent, toxic and ubiquitously distributed in the environment. These compounds are highly bioaccumulative and adversely affect the ozone layer in the atmosphere. As such, its widespread usage is a major cause of environmental and health concern. Therefore it is important to detoxify such compounds by environment friendly methods. In this work, for the first time rice husk supported platinum (RHA-Pt) and Titanium (RHA-Ti) catalysts were used to investigate the detoxification of chlorobenzenes and Chlorophenols in a glass capillary microreactor. High potential (in Kv range) was applied to expedite the activation of catalysts. The main advantage of this capillary reactor is in-situ generation of hydrogen for the detoxification of chlorobenzene and Chlorophenols. Various experimental conditions influencing detoxification were optimized. Reaction performance of capillary microreactor was compared with conventional catalysis. Only 20 min is sufficient to completely detoxify chlorobenzene and Chlorophenols in capillary microreactor as compared to 24 hrs reaction time in conventional method. The proposed method is simple, easy to use and suitable for the detoxification of wide range of chlorinated organic pollutants.

ملخص الرسالة

الاسم الكامل: عبدالإله احمد علي ثابت

عنوان الرسالة: إزالة سميه المركبات العضويه المكلورة عن طريق استخدام مفاعل ميكروي وتقديرها بواسطه جهاز الغاز الكروماتوجرافي (اللوني) / مطياف الكتلة

التخصص: كيمياء

تاريخ الدرجة العلمية: رجب 1434 هجرية

الملوثات العضوية المكلورة هي مركبات تتسم بالثبات والسمية والانتشار الواسع في البيئة. وهذه المركبات تتصف بقابليتها العالية لعملية التراكم الحيوي و تأثيرها السلبي على طبقة الأوزون في الغلاف الجوي. على هذا النحو، فإن استخدامها على نطاق واسع يعتبر السبب الرئيسي للاهتمام بها صحيا وبيئيا. ولذلك فمن المهم إزالة سمية هذه المركبات بطرق صديقة للبيئة. في هذه الرساله ولأول مره تستخدم حفازات البلاتين (RHA-Pt) و التيتانيوم (RHA-Ti) المدعمه بقشور الأرز في إزالة سمية مركبات البنزين المكلورة بواسطه مفاعل زجاجي شعري ميكروي (صغير جداً) اضافه الي تطبيق جهد عالي في نطاق الكيلوفولت لتسريع (تعجيل) نشاطيه الحفازات في التفاعل. الميزة الرئيسية لهذا المفاعل الشعري هي توليد(انتاج) الهيدروجين داخل المفاعل لإزالة سمية مركبات البنزين المكلورة. تم تحسين الظروف التجريبية المختلفة التي تؤثر علي إزالة السموم. كفائة (فعاليه) التفاعل في المفاعل الشعري الميكروي قورنت بطرق الحفز التقليديه .عشرون (20) دقيقه فقط كانت كافية لإكمال إزالة سمية مركبات البنزين المكلورة في المفاعل الشعري الميكروي مقارنة بـزمن تفاعل مقداره أربعة وعشرون (24) ساعه عند استخدم طرق الحفز التقليديه .الطريقه المقترحه بسيطه وسهله الاستخدام ومناسبه لإزالة سمية مجموعة واسعة من الملوثات العضوية المكلورة.

درجة الماجستير في العلوم

جامعة الملك فهد للبترول والمعادن

الظهران- المملكة العربية السعودية

CHAPTER 1

INTRODUCTION

1.1 Chlorinated organic compounds (COCs)

1.1.1 Description, uses, classification, impacts and examples of COCs

Chlorinated organic compounds (COCs) are a large class of synthetic and natural organic molecules that contain one or more chlorine atoms. They are one of the most versatile and widely used classes of compounds in the industrial world.[1]. For example; COCs are used in the composition of synthetic rubbers and shoes. They also create polymers used in packaging, and products like fluid pipes, furniture, fences, and so on. COCs can also be used as anesthetics, pesticide and herbicide, industrial solvents, and they are byproducts of several industries (oil refining, paper, plastics and adhesives manufacturing etc.). COCs can be classified into two different groups: aliphatic and aromatic. They have distinct chemical and physical properties depending on the number of chlorine atoms and other functional groups they contain .Chlorinated aliphatic compound refers to a substance containing an aliphatic chain of hydrocarbon in which at least one of the carbons bears a chlorine substituent rather than hydrogen. They are mainly used as starting materials in organic and pharmaceutical industries, solvents, refrigerants, monomers, etc. The most commonly used and widely distributed examples of chlorinated compounds include CFCs, vinyl chloride, trichloroethylene etc. Chlorinated aromatic

compound refers to a substance containing mesomeric π-electron system in a carbocyclic framework in which at least one of the ring carbon bears a chlorine substituent rather than hydrogen. These compounds are recognized as important starting materials and additives in the production of high-quality insecticides, fungicides, herbicides, dyes, pharmaceuticals, disinfectants, rubbers, plastics, textiles, plant growth regulators, heat-transfer medium, dielectric fluid, lubricants and solvents. The most common examples of chlorinated aromatic hydrocarbons include various chlorobenzenes, chlorophenols, polychlorobisphenol (PCB), DDT. .Chlorinated chemicals and solvents have increasingly played important roles in both industrial and agricultural sectors. The number of chlorine atoms or carbon atoms bonded and how they are arranged strongly determines the chemical and physical properties of these molecules. The importance of these chlorinated chemicals lies with the fact that chlorine bonds strongly to other elements and this makes chlorine an important ingredient and precursor in building new compounds. Unfortunately, this property is also one of the reasons why chlorinated compounds once formed, are hazardous. Due to this strong bond strength, it is hard to breakdown them and hence persists in the nature. Chlorinated compounds are persistent, toxic and ubiquitously distributed environmental contaminants. Chloro-containing compounds also adversely affect the ozone layer in the atmosphere. As such, its widespread usage is a major cause of environmental and health concern. Moreover, COCs are among the most widely distributed pollutants in wastewaters and contaminated ground waters.[2] Most COCs listed as priority pollutants by the U.S. Environmental Protection Agency (USEPA) [3]. Due to its lipophilic nature (easily concentrate in fats of animals, which lead to biomagnifications), polychlorinated aromatic compounds which are environmentally

stable and persistent in nature tend to bioaccumulate in the food chain[4] Bioaccumulation indirectly effect human as these compound residues are detected in food and human adipose tissues, milk, and serum fat.[5]. These chemicals elicit a broad spectrum of toxic and mutagenic biological responses. Such responses include dermal toxicity, immunotoxicity, carcinogenicity, and adverse effects on the reproductive and endocrine systems. This thesis focus at the dechlorination of the following chlorinated aromatic compounds (CACs) chlorinated benzenes (CBs) and chlorinated phenols (CPs).(COCs) have been the focus of intensive concern due to their highly refractory nature, bioaccumulation and toxicity. Chlorinated benzene consist molecules as monochlorobenzene, 1,2-dichlorobenzene (1,2-DCB), 1,3-dichlorobenzene (1,3-DCB), 1,4-dichlorobenzene (1,4-DCB), 1,2,4-trichlorobenzene(1,2,4-TCB), 1,2,3,4,5,6-hexachlorobenzene (HCB). It is insoluble in water, slightly soluble in alcohol, and very soluble in benzene an solvents like petroleum ether, carbon disulfide, chlorinated aliphatic and aromatic hydrocarbons [6]. chlorinated phenol consist molecules like monochlorophenol (MCP), 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichloro-Phenol (2,4,5-TCP), 2,4,6-Trichlorophenol (2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), 2,3,5,6-tetrachlorophenol (2,3,5,6-TeCP), and pentachlorophenol (PCP). All these compounds are solid except 2-chlorophenol that is liquid at room temperature. Chlorophenols, a major group of pollutants, they are present in the environment from many industries, including petrochemical , coal gasification, dye-manufacturing, paper, solvents, and pharmaceutical industries, and also from agricultural activities, since many of them are used extensively in pesticides, fungicides and, herbicides, they are causing serious environmental problems because of their toxicity and resistance to

degradation[7.8]. Most CPs are hazardous pollutants in the environment which have been listed as priority pollutants by (US.EPA) [3]. Moreover, polychorophenols are considered as possibly carcinogenic to humans by the IARC (International Agency of Research on Cancer).[9]

1.2 Catalytic hydrodechlorination (HDC) of COCs

1.2.1 Description, Advantages, Catalysts, Microreactor

Several treatment methods have been developed to eliminate COCs, such as Oxidation methods and incineration [10,11]. mechanochemical methods, and Reductive methods such as electrochemical [12], photochemical [13], ultrasonic [14], microbial [15] and radiolytic and thermal [16] reductive methods have been developed. Besides reductive methods, bioremediation using natural biological activity by means of aerobic and anaerobic biodegradation of chlorinated compounds have also been extensively studied [17-19]. Among them, catalytic hydrodechlorination (HDC), which involves the reductive cleavage of a C-Cl bond by highly reactive atomic hydrogen ([H]), is a green (environmentally friendly) and cost-effective technique. So far as, the effective degradation of various COCs, including chlorobenzenes, and chlorophenols, has been successfully achieved [20]. It is one of the most promising alternatives method for the detoxification of COCs, HDC operates in liquid or gas phase using different catalytic systems yielding none or partially chlorinated hydrocarbons and HCl as products [21].

HDC is the reaction of a chlorinated organic compound, R-Cl, with hydrogen to form a carbon-hydrogen bond and HCl. It can be represented by the following chemical equation.

R-Cl + H-H → R-H + H-Cl (1.1)

Equation 1-1 Scheme of hydrodechlorination reaction

Moreover, this reaction can be done in mild conditions at ambience, low or high temperature and pressure, forms no harmful side-products are observed and could eventually be selective towards chloride removal.[21,22]

HDC has many Advantages as (1) non-destructive technology, (2) produce environmentally hydrocarbon compounds which can be eliminated or recycled, (3) ability to operate at mild conditions, (4) high rate of reaction, (5) No harmful side-products like dioxins, furans, (6) less sensitivity to pollutant concentrations and (7) allows selective removal of Chlorine from variety of chlorinated organic compounds or mixtures. Unlike other techniques mentioned above, HDC is simple, efficient and clean method. The hydrogen source in the HDC reaction can be molecular hydrogen (H_2) or any other hydrogen donor such as formic acid, and its salts or alcohols isopropanol, hydrazine etc [23-25]. This reaction is quite exothermic and thus requires the presence of a catalyst to drive it to completion. The reaction also requires selective cleavage of C-Cl bond and therefore requires selective catalysts. Several hydro-dechlorination catalysts have been reported in literature [26, 27]. The HDC reactions can be catalyzed using heterogeneous or homogeneous catalysts. Catalysis is an integral component in any green processing technology serving as an important tool to support sustainable development. Catalysis

play an important role in hydrodechlorination reaction both fo the purpose of synthesis of raw materials or waste treatment. It used for detoxification of chlorinated organic compounds COCs [23-26]. In previous years, much effort has been focused in the study of the catalytic hydrodechlorination of COCs by catalysts based on different metals and supports. Generally metals such as palladium, ruthenium, rhodium, iridium, rhenium, titanium, Platinum, and Raney nickel [28-31] were employed as the catalysts for transfer hydrogenolysis. Alumina, activated carbon [28], Ni–Mo/C [32], and silica are among the catalyst supports most commonly used in the HDC reaction. Use of molecular hydrogen (H_2) has been investigated as a donor of hydrogen in the hydro dechlorination process using nano-catalysts which have large surface/bulk atomic ratio that exhibit unique properties has found application in catalysis [33,34] and electrocatalysis [35,36]. Various metal nanoparticles like tin, nickel, palladium, and titanium, have been developed by scientists for special technological applications [37]. These nanoparticles can be viewed as nanoelectrodes carrying and transferring electrons in electrocatalysis. For supported metal NPs, the catalytic activity of the NPs not only depends on the size of the particles but also on the nature of the support and the preparation method of the support. The support plays a significant role in the activity and the stability of the catalysts [38]. Rice husk (RH) is an agricultural waste and the ash contains about 92–95% silica (SiO_2). It is highly porous and lightweight, with high surface area. Many publication reports the using of rice husk ash as catalyst support for metals [37]. HDC processes can be performed in batch reactors for small and medium-scale processes (producing specialty chemicals, fine chemicals and pharmaceuticals), and/or continuous-flow reactors for large-scale processes (treating bulk hazardous chemicals). Conventional method HDC using a direct

hydrogen gas supply had been performed in bulk scale to compare with the proposed method. For Conventional method the HDC experimental set up is as shown in Figure 1b. The miroreactors used are miniaturized reactor systems with reactor channel characteristic dimensions in the sub-millimeter range. These devices have been investigated for a number of model gas–surface catalytic reactions, liquid-phase, gas–liquid reactions as well as some selected commercial demonstrations like partial oxidation reaction in fuel cells and fine chemicals production [39]. Compared to conventional laboratory and chemical vessels, microreactors having much higher surface to volume ratio, provide excellent heat and mass transfer and hence result in better control of reaction conditions. Other advantages following the small dimensions include improved safety and portability and reduced reagent consumption. A glass capillary-based microreactor (as shown in Fig. 1a) had been fabricated for this study. Glass is chemically inert, optically clear and nonporous hence making it a suitable material as a reaction chamber [40, 41]. The present study investigates detoxification of chlorinated aromatic compounds over Silica–Platinum and Silica–titanium supported catalysts under mild condition by using buffered solutions in a capillary-micro- reactor containing a mixture of reactants. In our approach, the reaction device is a glass capillary connected to a power supply as shown in (Fig. 1a). Within the capillary, a potential is applied which enhance the efficiency of the reaction. Compared with conventional HDC, a higher dechlorination/detoxification of aromatic chlorides is expected under optimized reaction conditions. A lot of methods through analytical techniques utilized in the quantitative determination of COCs have been reported [7,8,9,20,28,32,40]. GC coupled with mass spectrometric detection may provide better resolution and ease of identification of peaks.

1.3 OBJECTIVES

This main objectives of the thesis are;-

To design and investigate a new capillary microreactor for hydro-dechlorination reaction of organochlorine contaminants in water sample.

I. Design and optimization of capillary microreactor method.

II. Synthesis and characterization of supported catalysts

III. Investigation of hydro-dechlorination reaction in microreactor using electro-catalysis and conventional method.

1.4 PROBLEM STATEMENT

Numerous organochlorine contaminants detected in groundwater and surface water include chlorinated aromatic, polychlorinated biphenyls, hexachlorocyclohexanes and chlorophenols. Nowadays; increasing attention is been paid to the preservation of water resources and their quality. As a consequence, the removal of toxic organic pollutants from wastewaters has attracted significant research efforts. Chlorinated organics are among the most widespread pollutants encountered in industrial wastewaters and receiving water systems [42]. Special attention has been paid to chlorinated aromatic compounds because they are used in a number of important industrial processes such as the production of germicides, algaecides, fungicides, herbicides, dyes, wood protectors and plant growth regulators. Chlorinated aromatic compounds also formed during wood

pulp bleaching and water chlorination. Due to their high toxicity, strong odour emission and persistence in the environment and suspected carcinogenity and mutagenity to living organisms, these compounds are recognized as hazardous substances due to their toxicity [43]. Chlorinated aromatic compounds (CACs) can cause serious environmental problems because they are difficult to be decomposed biologically. With most COCs listed as priority pollutants by the U.S. Environmental Protection Agency. So, there is urgent need to develop efficient and cost-effective methods to detoxify and destroy them [20].

CHAPTER 2

LITERATURE REVIE

2.1 Section Chlorinated organic compounds (COCs)

Chlorophenols (CPs) are used both as intermediates and end products in the manufacture of herbicides, dyes and plant growth regulators. CPs act as antisapstain agent and are thus used for the treatment and protection of wood from fungi. In recent years, CPs is called upon as priority environmental pollutants. Its presence in the environment is mostly through water contamination [7]. CPs can cause serious environmental problems. They are difficult to be decomposed by bio-degradation. Exposure to CPs can lead to kidney, liver, blood and central nervous system damage. Another class of polychlorinated aromatic compounds of concern is the polychlorinated biphenyls (PCBs). PCBs were used in plasticizers formulation of coatings, inks, adhesives, flame retardants and pesticides extenders. Although the use of PCBs have been banned in many countries and PCB containing transformers and capacitors replaced [44], these chemicals still pose a public threat due to their persistence in the environment. PCBs are rapidly absorbed from the gastrointestinal tract, and are distributed and accumulated in the liver and adipose tissues. The compounds have serious ecologically harmful effects and are implicated as potent carcinogens.

A class of organochlorine compound is the hexachlorocyclohexane (HCH). Initially it was synthetically produced as industrial insecticides and for medical usage to treat

scabies and lice. All agricultural use of Lindane, a gamma isomer of HCH, is released into the environment during and after agricultural application through vaporisation into the atmosphere (estimated at 12-30%), where it has long-range transport potential and can be deposited by rainfall. Lindale in soil can leach to surface and even ground water, although the potential is low, and can bioaccumulate in the food chain. In fact, the most widespread exposure of the general population to lindane results from agricultural uses and the intake of contaminated foods, such as produce, meats and milk [5].

Chlorinated toluene's are especially used for the industrial production of pesticides and dyes. Chlorinated organic solvents such as p-chlorotoluene, used as intermediates in chemical processes are listed as one of the many contaminants that should be tested in drinking water. p-chlorotoluene may be released to the environment in emissions and effluents from sites of its manufacture or industrial use, from venting during storage and transport, and from disposal of industrial waste products which contain this compound (i.e. spent solvent). p-chlorotoluene may be formed in the environment as a result of photodegradation of p-chlorobenzyl chloride, a chemical intermediate. Probable route of human exposure to p-chlorotoluene is inhalation of contaminated air and to ingestion of contaminated drinking water.

2.2 Detoxification methods of COCs

The harmful characteristic of such chemicals discussed made it mandatory to find and develop new ways of removing/ detoxification from the environment. Several treatment

methods have been developed. Oxidation methods and incineration [10, 11] employed as means of degradation of these compounds have unfortunately resulted in the formation of some noxious chemicals such as dioxins. Therefore reductive methods can be seen as viable alternative methods. Reductive methods such as electrochemical [12], photochemical [13], ultrasonic [14], microbial [15], and radiolytic and thermal [16], reductive methods have been developed. Besides reductive methods, bioremediation using natural biological activity by means of aerobic and anaerobic biodegradation of chlorinated compounds have also been extensively studied [17-19]. Bioremediation techniques are typically more economical than traditional methods such as incineration, and some pollutants can be treated on site, thus reducing exposure risks for cleaning personnels, or potentially wider exposure as a result of transportation accidents. However it will not always be suitable, as the range of contaminants on which it is effective is limited, the time scales involved are relatively long, and the residual contaminant levels achievable may not always be appropriate. Furthermore chlorinated contaminants have been known to resist microbial attack [45].

2.3 Catalytic hydrodechlorination (HDC) of COCs

Chemical treatment by catalytic hydrodechlorination (HDC) has been proven to be a convenient and effective method for the decontamination of chlorinated compounds from water bodies. HDC is the reaction of a chlorinated organic compound (COCs), R-Cl, with hydrogen [H_2] to form a carbon-hydrogen bond and HCl as show in Eqn 1:

$R\text{-}Cl + H_2 \rightarrow R\text{-}H + HCl$

This reaction is exothermic and thus requires the presence of a catalyst to drive it to completion. The reaction also requires selective cleavage of C-Cl bond and therefore requires selective catalysts. Several hydrodechlorination catalysts have been reported in literature [26, 27]. Many catalytic hydrogenation with molecular hydrogen [H_2] actually involves atomic hydrogen dispersed in and over the catalyst [23].

Transfer hydrogenolysis is a lesser known possibility of achieving reduction with the aid of organic molecule as the hydrogen donor in the presence of a catalyst. [23] Generally metals such as palladium, ruthenium, rhodium, iridium, rhenium, titanium, Platinum, and Raney nickel [28-31], were employed as the catalysts for transfer in hydrogenolysis. Alumina [28, 46-48, 53-55], activated carbon [28, 49, 50, 53-55], Ni–Mo/C [32] and silica [50-52] are among the catalyst supports most commonly used in the HDC reaction. The hydrogen source in the HDC reaction can be molecular hydrogen (H_2) or any other hydrogen donor such as formic acid, and its salts or alcohols isopropanol, hydrazine etc. [2,23,24,56]. This reaction can carried out under mild conditions at ambience temperature and pressure. The low molecular weight of molecular hydrogen gas brings about its properties of high diffusibility, highly ignitable thus presenting considerable hazards. As such, transfer hydrogenolysis which is done without the need for hydrogen pressure vessels or containment offers considerable advantages over conventional methods of catalytic hydrodechlorination. As discussed by Johnstone and Wilby [23], the reaction involving hydrogen transfer, hydrogen can exist either as a proton, atom or hydride depending on the reagent and conditions. For transfer hydrogenolysis, it is necessary to use suitable catalyst and hydrogen donor. In recent years, catalytic dechlorination

methods have been developed including transfer hydrogenation by means of hydrogen donors such as metal hydrides, formic acid and its salts and alcohols which use water or methanol as solvents [23]. H_2 will be used as a donor of hydrogen in the HDC process using supported catalysts.

2.4 Detoxification of CBs and CPs over supported catalysts

Nano catalysts have large surface/bulk atomic ratio which exhibit unique properties has found application in catalysis [33,34] and electrocatalysis [35,36]. Various metal particles like tin, nickel, palladium, and titanium, have been developed by scientists for special technological applications [37]. These particles can be viewed as electrodes carrying and transferring electrons in electrocatalysis. For supported metal, the catalytic activity not only depends on the size of the particles but also on the nature of the support and the preparation method of the support. The support plays a significant role in the activity and the stability of the catalysts [38,53-55]. Rice husk (RH) is an agricultural waste and the ash contains about 92–95% silica (SiO2). It is highly porous and lightweight, with high surface area (225.4 m^2/g). Many publication reports the use of rice husk ash as catalyst support for metals, such as tin, ruthenium, gallium, indium, iron, aluminum, and titanium [37, 57-59]. Therefore the present study uses Silica– platinum and Silica–titanium supported particles for the detoxification of chlorinated aromatic compounds.

2.5 HDC reaction in a capillary-microreactor

HDC processes can be performed in batch reactors for small and medium-scale processes (producing specialty chemicals, fine chemicals and pharmaceuticals), and/or continuous-flow reactors for large-scale processes (treating bulk hazardous chemicals). Few studies used microscale reactors for the detoxification of organic pollutants, Jahnisch et al, reviewed that the reaction yield increase by 10% when compared to conventional reactor processes [60]. Recently, microfluidic device was reported by Maruyama et al and S. Tadepalli et al. [7, 61] G. N. Jovanovic at el developed a microreactor for the degradation of p-chlorophenol (PCP) to obtain the dechlorination of PCP in a continuous-flow microreactor system made of iron plates. Moreover, C. Basheer et al. designed, developed and used a capillary-microreactor which made from Pyrex glass for Suzuki coupling reactions and also for oxidation of glucose with a porous gold catalyst. They reported that the glass capillary microreactors are simple, low cost, easier to use and provide high reaction rate and high efficiency than photolithographic microfluidic devices and conventional large-scale reactors [40,41]. As well as compared to conventional laboratory and chemical vessels, microreactors having much higher surface to volume ratio, provide excellent heat and mass transfer and hence result in better control of reaction conditions. Other advantages following the small dimensions include improved safety and portability and reduced reagent consumption. Glass is chemically inert, optically clear and nonporous hence making it a suitable material as a reactionchamber [40, 41]. A glass capillary-based microreactor (as shown in Fig. 1(a) and 2 had been fabricated for this study.

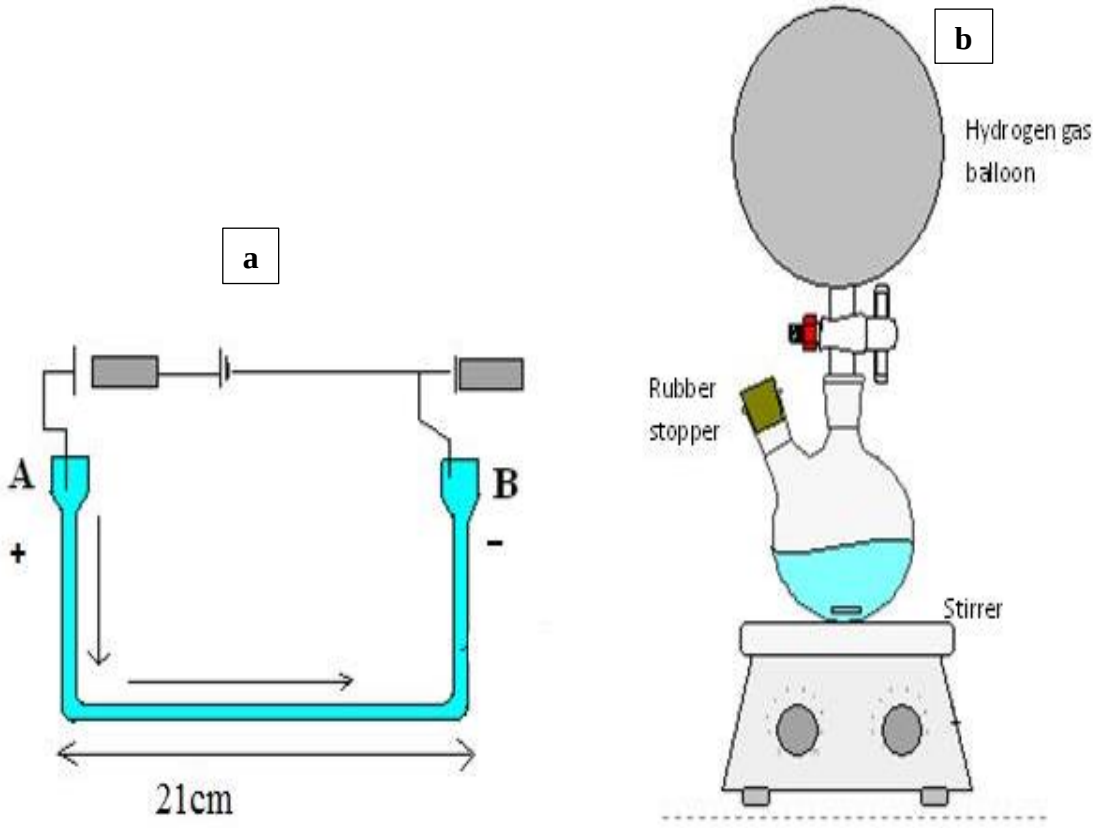


Figure 2-1 Schematics of (a) the glass capillary microreactor for transfer hydrogenolysis reaction (b) Conventional experimental set up for hydrodechlorination reaction with external supplied hydrogen gas source

CHAPTER 3

Research Methodology

3.1 Materials

Platinum chloride ($PtCl_2$) was used as the source of Platinum and Titanium dioxide (TiO_2) as the source of Titanium. Other materials used were nitric acid (Q Rec, 65%), sodium hydroxide pellets (R&M Chemicals, 99%), acetone (Q Rec,99.5%), cetyltrimethy- lammonium bromide (CTAB, Riedel-de Haen, 98%) and methylene blue (Sigma Aldrich).Rice husk was obtained from a local rice milling company in Penang. 8270 MegaMix (RESTEK) 100ppm, Heptane, 1,2-dichlorobenzene (1,2-DCB)(Fisher Scientific, 99.2%), 1,3dichloro,benzene (1,3-DCB)(Fluka,99%), 1,4-dichlorobenzene (1,4-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB)(Scharlau,HPLC grade, 99%), hexachloro-benzene(HCB),(Sigma-Aldrich, 99%), 2-chlorophenol (2-CP) 2,4-dichlorophenol (2,4-DCP), 2,4,5-trichloro-phenol (2,4,5-TCP), 2,4,6-trichlorophenol|,(2,4,6-TCP), 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP), 2,3,5,6-tetrachlorophenol (2,3,5,6-TeCP), and pentachloro-phenol(PCP), (Chem Service >98%), Phenol(Flucka ,99.5%) and Benzene(Sigma-Aldrich, ≥99.0%). All chemicals were of AR grade and used directly with no further purification.

3.2 Synthesis of RHA-Pt and RHA-Ti Supported Catalysts

30g of clean rice husk (RH) was stirred with 750 mL of 1.0 M HNO_3 at room temperature for 24 hrs. The cleaned RH was washed with copious amount of distilled water to constant pH, than dried in an oven at 100 ◦C for 24 hrs and burned in a muffle furnace at 600 ˚C for 6 h so as to obtain white rice husk-ash (RHA) [37]. About 3.0 g of RHA was added to 350 mL of 1.0 mol L^{-1} NaOH in a plastic container and stirred for 24 hrs at room temperature to get sodium silicate solution. About 3.6 g of CTAB (1:1.2, Si: CTAB molar ratio) was added into the sodium silicate solution and stirred to dissolve completely. This solution was titrated with 3.0 mol L^{-1} HNO_3 at a rate of ca. 1.0 mL min^{-1} with constant stirring until pH 3.0. The resulting gel was aged for 5 days, then filtered and washed thoroughly with distilled water, finally washed with acetone. The gel was dried at 110 ˚C for 24 hrs ground to fine powder and was calcined at 500 ˚C in a muffle furnace for 5 hrs, than labeled as RHA-silica powder .Same procedure followed for the preparation of RHA-silica Solution of 10 wt. % Pt of ($PtCl_2$) which dissolved in 50 mL of 3 mol L^{-1} HNO_3 and titrated .similarly, Solution of 10.0 wt. %Ti of (TiO_2) dissolved in 50 mL of 3 mol L^{-1} HNO_3 was titrated. The resulting gels were treated as described above.The resulting powder were labeled as RHA-Pt and RHA-Ti

3.3 Catalysts Characterization

The prepared samples were characterized using Fourier transform infrared (FTIR) spectroscopy , N_2 adsorption–desorption analysis, Field-Emission Scanning Electron Microscope (FESEM), and Energy dispersive spectrometry (EDX).

3.3.1 FT-IR spectral analysis

The FT-IR analysis was carried out in Nicolet 6700 FT-IR using the KBr pellet method. Figures. (1-3) show the FT-IR spectra of the catalysts RHA-Ti and RHA-Pt and RHA-SiO_2, TiO_2 and $PtCl_2$ obtained in the wavenumber range 400–4000 cm^{-1} .The broad band in the range 3471–3455 cm^{-1} is due to the stretching vibration of O–H bonds in Si–OH and the HO–H of water molecules adsorbed on the materials surface [37, 42]. The band at 1628–1650 cm^{-1} is due to the bending vibration of H_2O, trapped in the silica matrix. The band around 1104 cm^{-1} was shifted to lower wave number for metal incorporated RHA. The band at 1090–1104 cm^{-1} is attributed to asymmetric Si–O–Si stretching vibration, from the structural siloxane bond. The band at 971.8 cm^{-1} can be attributed to the symmetric stretching vibration of Si–OH.[37] The intensity of this peak decreased in RHA-Ti and appears as a shoulder. This might indicate that some metal ions are attached on the surface of the silica as Si–O–M from the original Si–O–H or Si–O–Si silica structure. The absorption bands at about 465 and 470.5 cm^{-1} are due to Si–O–Si bending vibrations. [37] The bands at 800-802 cm^{-1} are due to the deformation and bending modes of Si–O–Si.

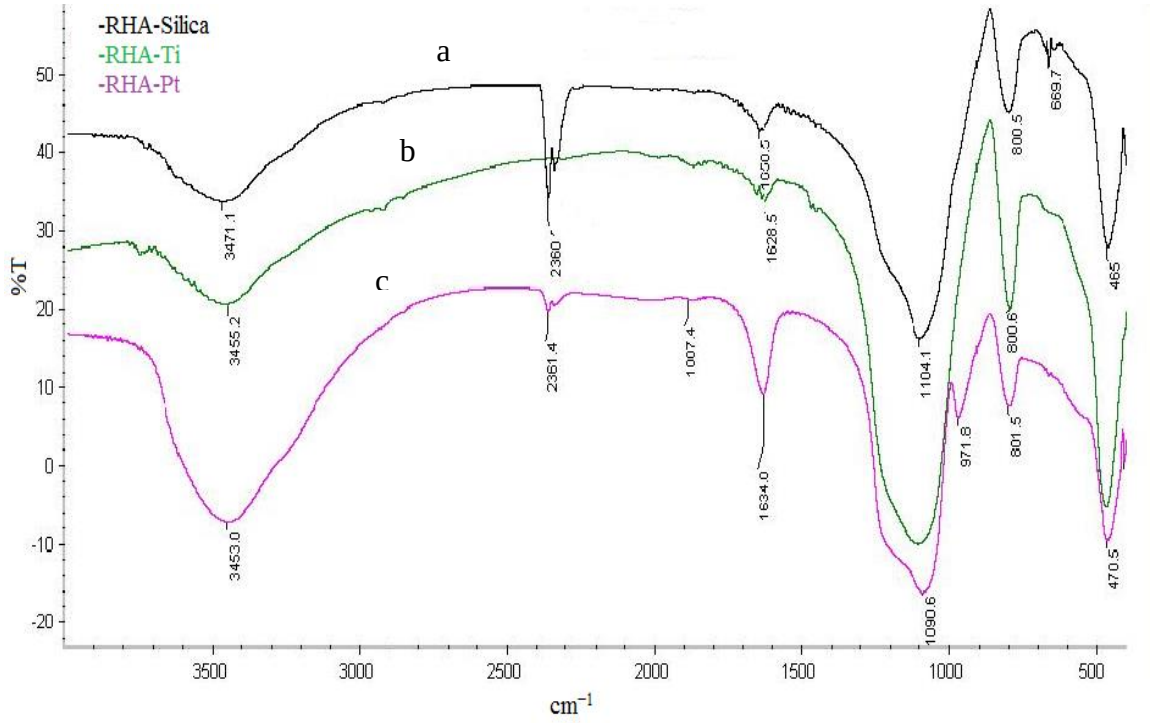


Figure 3-1.The FT-IR spectra of RHA silica and metal modified silica by loading10% (Ti and Pt) (a) RHA-SiO_2, (b) RHA-Ti, (c) RHA- Pt.

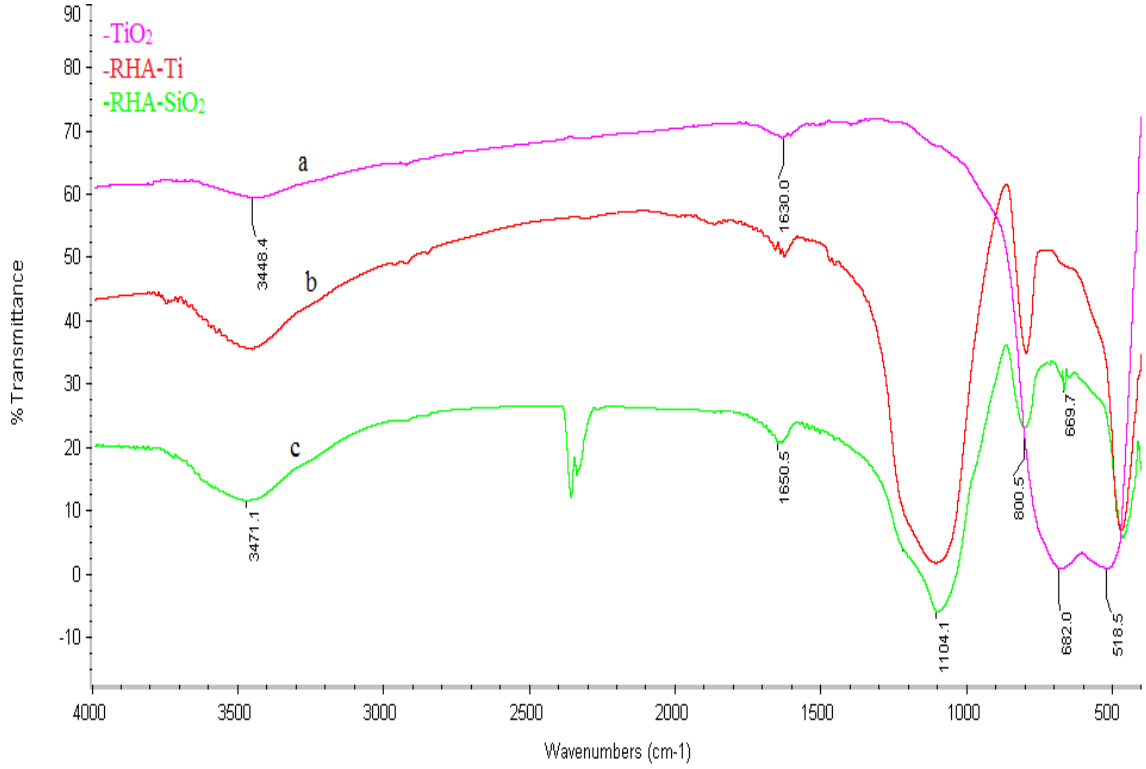


Figure 3-2 FT-IR spectra of (a) TiO_2, (b) RHA-Ti (c) RHA-SiO_2

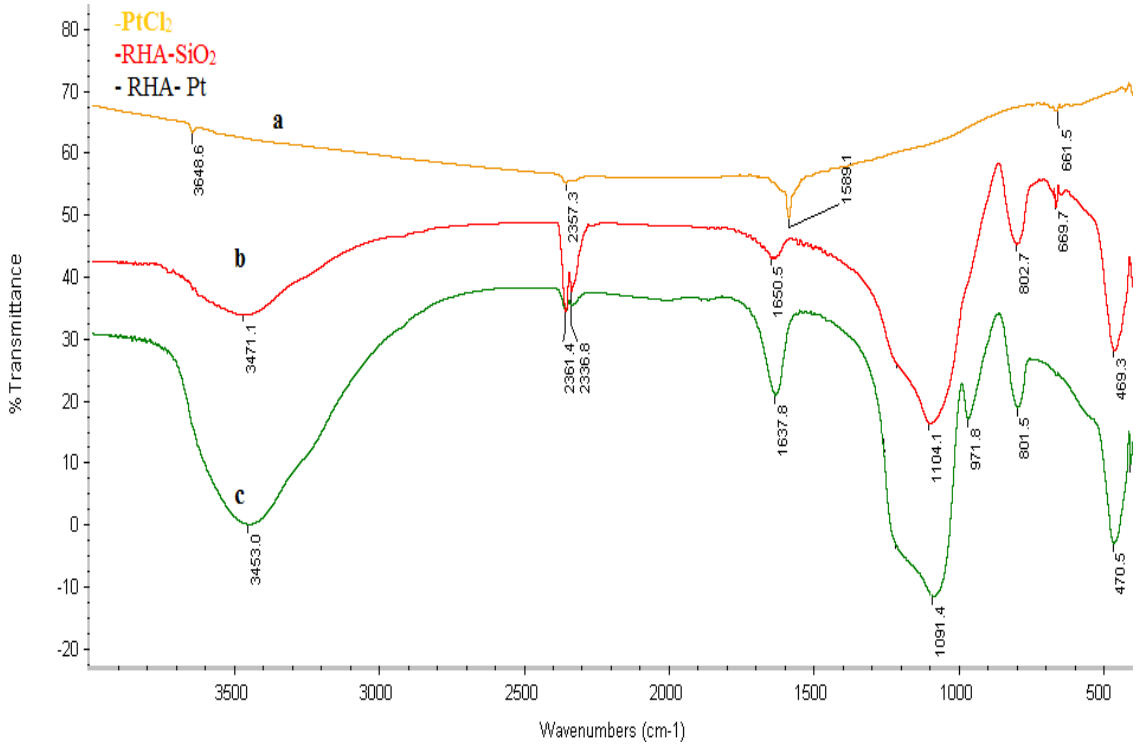


Figure 3-3 FT-IR spectra of (a) $PtCl_2$, (b) RHA-SiO_2, (c) RHA-Pt

3.3.2 N_2 adsorption–desorption analysis

The specific surface area, pore volume and pore size distribution of the prepared catalysts were carried out using N_2 adsorption–desorption on a Micromeritics ASAP 2020 volumetric instrument. Nitrogen sorption isotherms were performed at liquid nitrogen temperature (-195.786 °C). The N_2 adsorption–desorption isotherm of RHA-silica, RHA-Pt and RHA-Ti are shown in Figure 4. The surface area, pore diameter and pore volume were calculated using Barret–Joiner–Halenda (BJH) model and the results are displayed in Table.1 the average mesopore size was for all catalysts around 4 to 4.85 nm. As shown in Table.1. We see that RHA-silica have high surface area of (225.4306 m^2/g) while, RHA-Ti catalyst is associated BET surface area and pore volume of with (12.6548 m^2/g) and (0.012738 cm^3/g) respectively The incorporation of Ti into silica reduced its surface area and. pore volume compared to RHA-silica, due to the pore blocking by the agglomerated particles.[58]. Whereas in the RHA-Pt supported catalyst the incorporation of Pt into silica matrix increased its surface area(538.0725 m^2/g) and. pore volume(0.637532 cm^3/g) compared to that of the support RHA-silica .this may be the Pt particle were well dispersed within the silica matrix [37].

Table 3-1 The nitrogen adsorption–desorption analysis parameters of materials

Catalyst	**BET Surface Area (m^2/g)**	**Pore Volume (cm^3/g)**	**Average Pore Size (nm)**
RHA-silica	225.4306	0.273179	4.84725
RHA-Pt	538.0725	0.637532	4.73938
RHA-Ti	12.6548	0.012738	4.02638

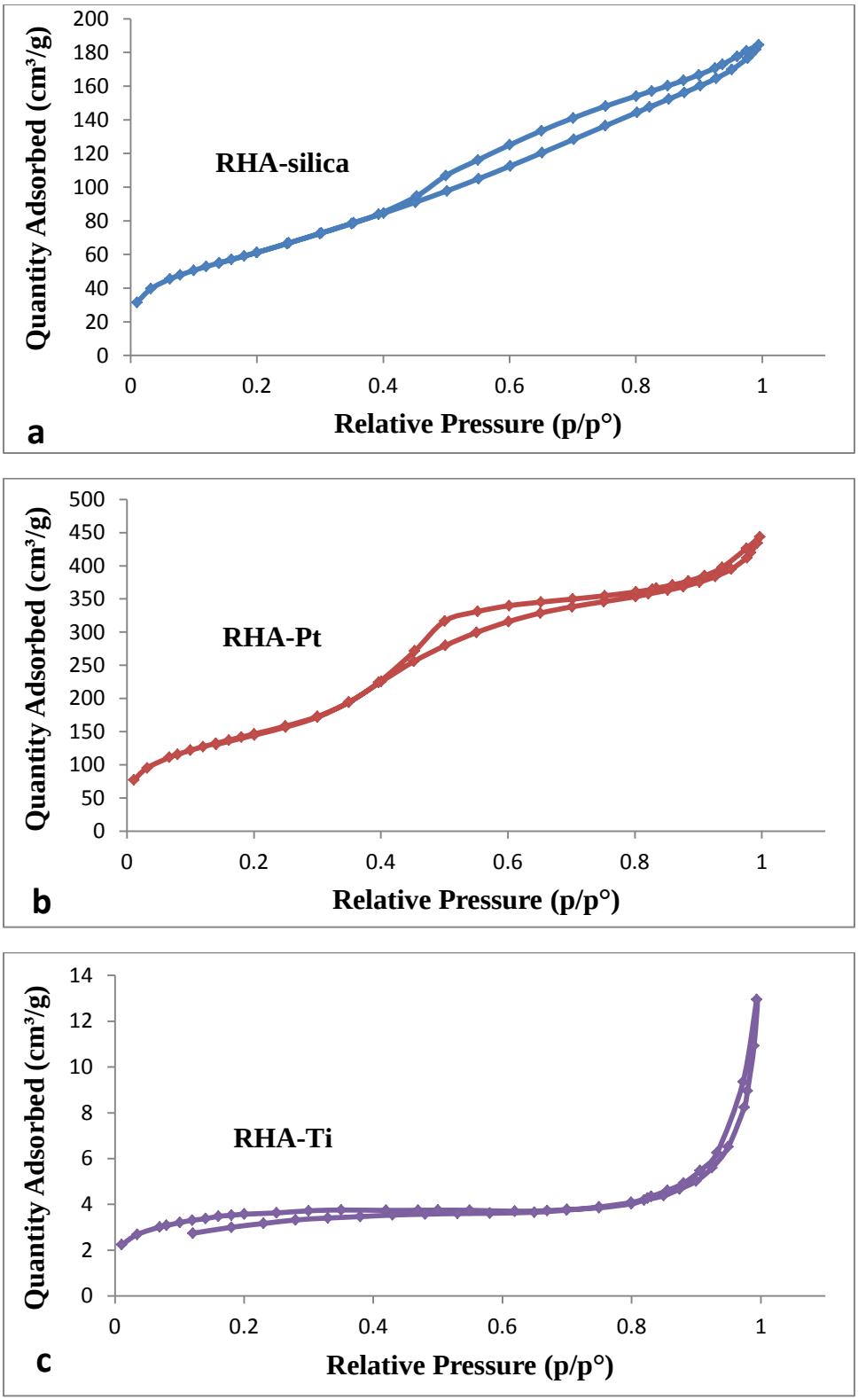


Figure 3-4 The nitrogen adsorption–desorption analysis of materials (a) RHA-silica(b) RHA-Pt (c) RHA-Ti

3.3.3 SEM and EDX analyses

Field-Emission Scanning Electron Microscope (FESEM) (Tescan Lyra-3) was used to investigate the surface morphology and the general morphological features of the prepared RHA-silica, RHA-Pt and RHA-Ti particles. The EDX measurements were also used to confirm the percentage, the atomic ratio, of the components on the prepared catalysts surface. RHA-Ti, RHA-Pt and RHA-silica specimens were examined FESEM micrographs of the RHA-silica shown in Fig 5. show the FESEM images of (a) RHA-silica sample and (b) the area of the RHA- silica sample from which EDX is measured. These images show that the RHA-silica particles have Flakes structure. These micrographs clearly illustrate the porous structure of RHA-silica. Fig 6 shows the Energy dispersive X-ray (EDX) spectrum of the RHA- silica and Inset which illustrates the percentages of the RHA- silica component (Si and O) in the sample. FESEM micrographs of the catalyst are shown in Fig.7 (a) and (b). These images show the morphology of the RHA-Ti particles that have rod-like morphology and the surface exhibit less porous as compared to RHA-silica. EDX measurments confirmed the precence of Ti, Si and O as illustrated on Fig 8 which shows the EDX spectrum of RHA-Ti, Inset is th percentages of the RHA- Ti component in the sample and the SEM of the area of the RHA-Ti sample from which EDX is measured. Fig. 9 show the FESEM image of RHA-Pt morphology (a)500nm and (b) 2µm. The Pt particles were dispersed and loaded on the surface of RHA. The RHA-Pt particles have spherical stretcher and surface exhibit porous. Fig 10. show the EDX spectrum of RHA-Pt catalyst; Inset is the percentages of the RHA- Pt component in the sample and the SEM of the area of the RHA-Pt sample from which EDX is measured.

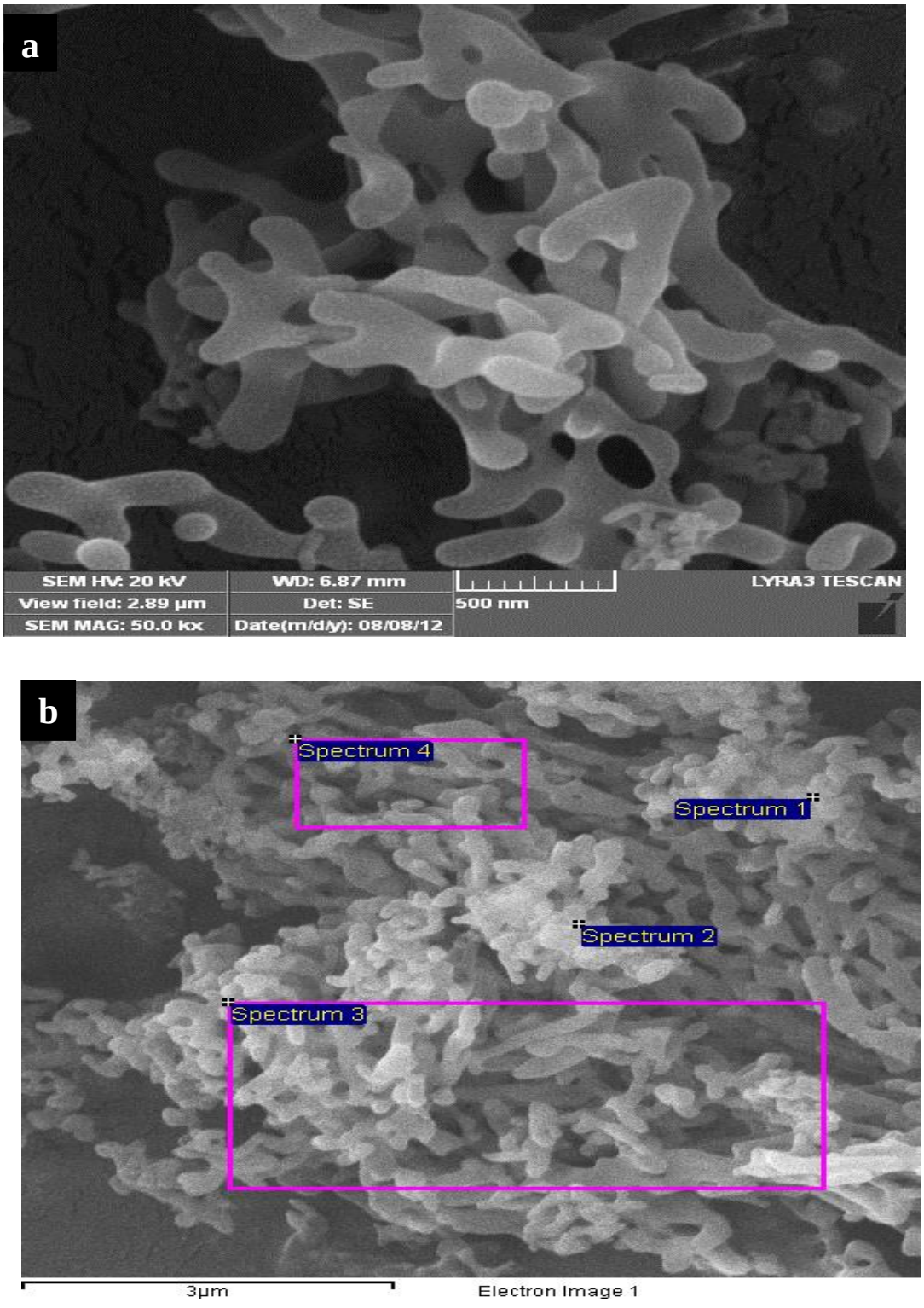


Figure 3-5 The FESEM image of (a) RHA- silica (b) is the SEM of the area of the RHA- silica sample from which EDX is measured

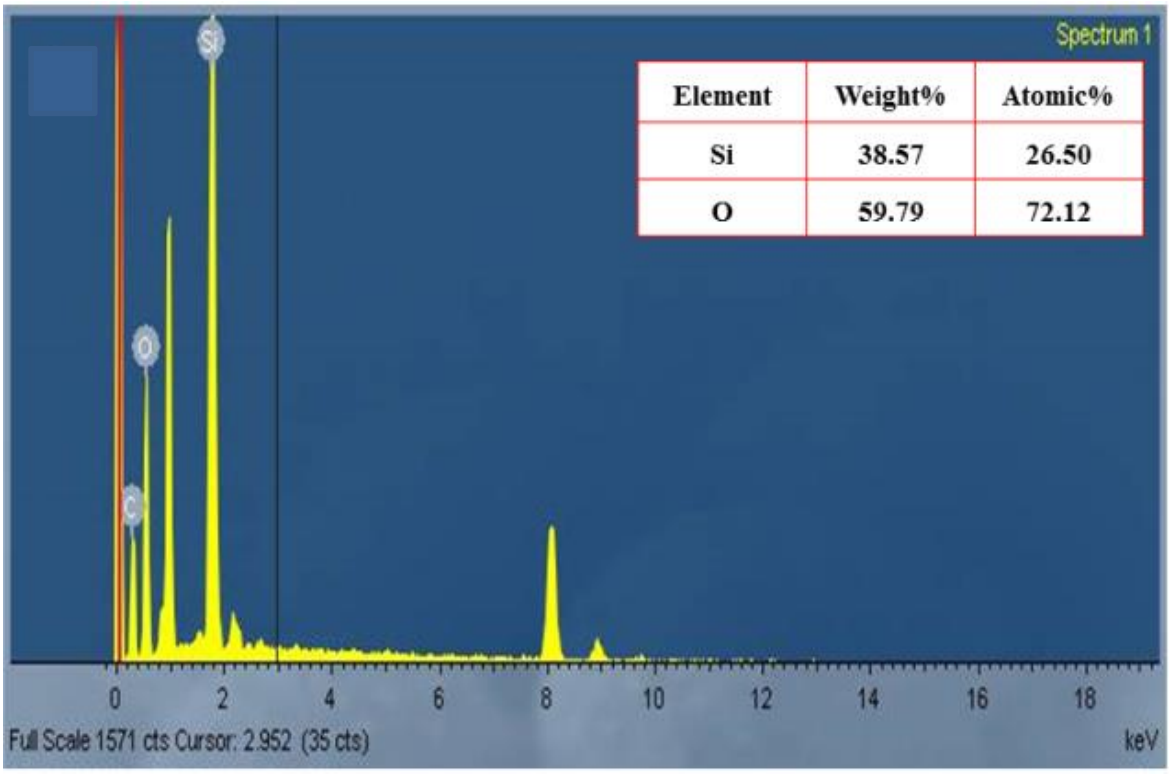
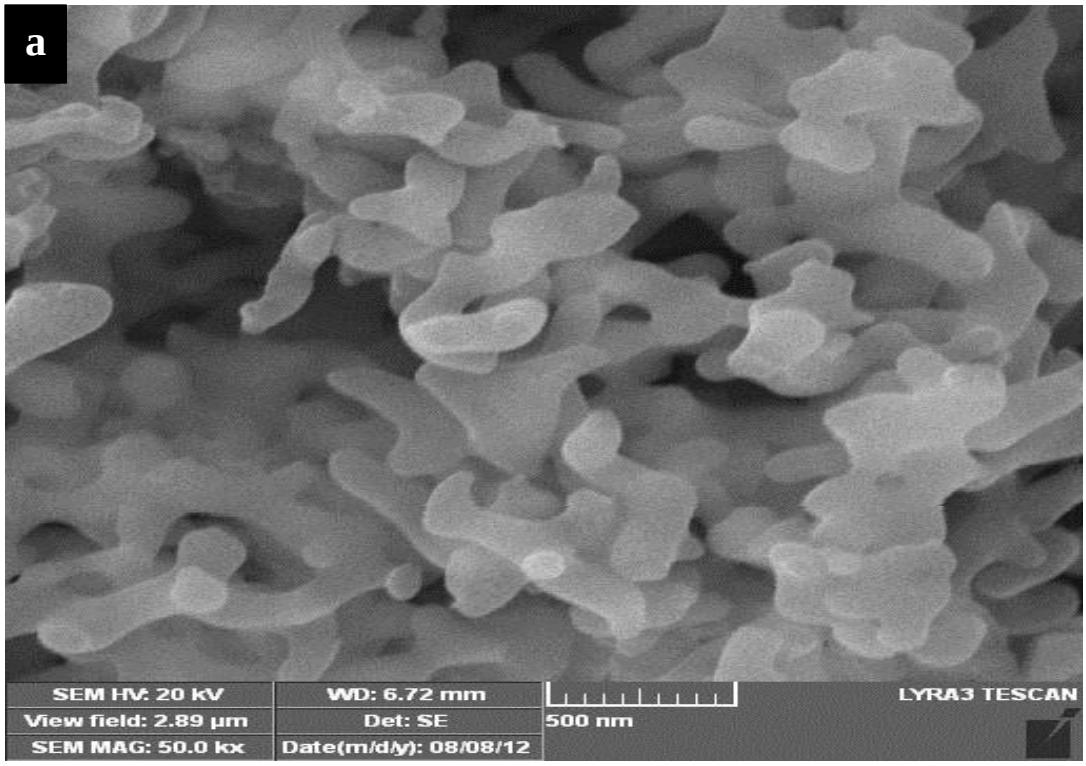


Figure 3-6 EDX spectrum of RHA- silica (a): Inset is th percentages of the RHA-silica component in the sample



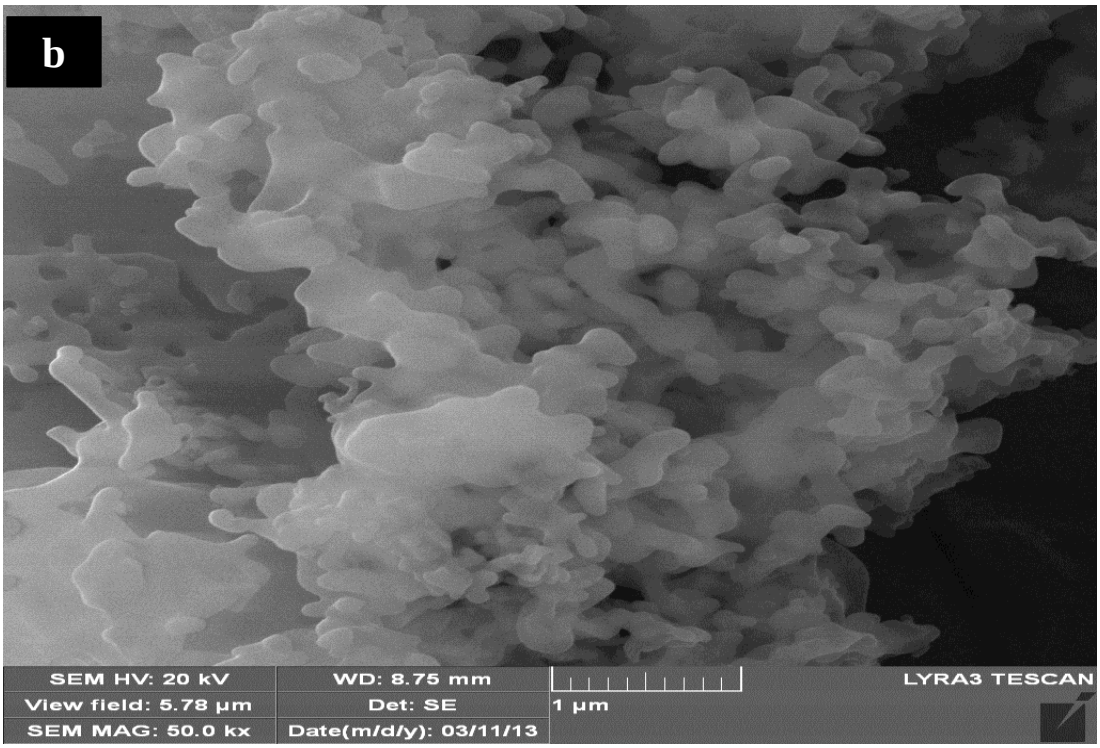
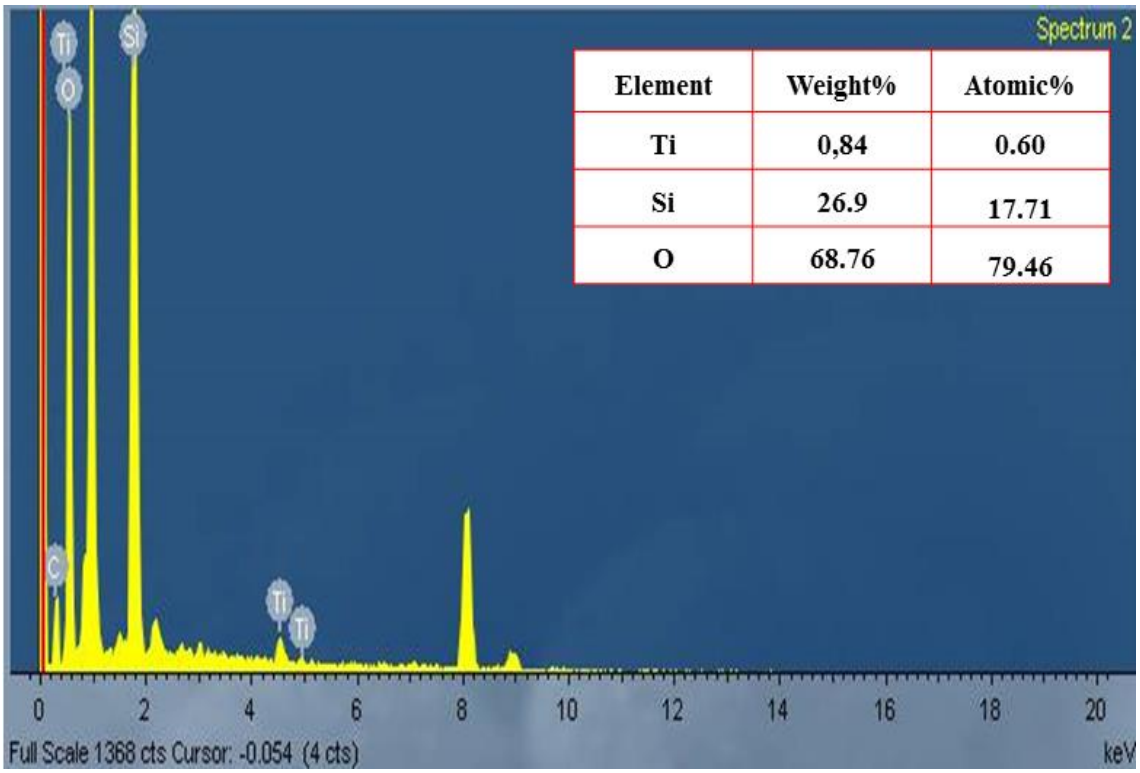


Figure 3-7 The FESEM image of RHA-Ti (a) 500nm and (b) 1µm



Element	Weight%	Atomic%
Ti	0,84	0.60
Si	26.9	17.71
O	68.76	79.46

Figure 3-8 EDX spectrum of RHA-Ti. Inset is th percentages of the RHA-Ti component in the sample

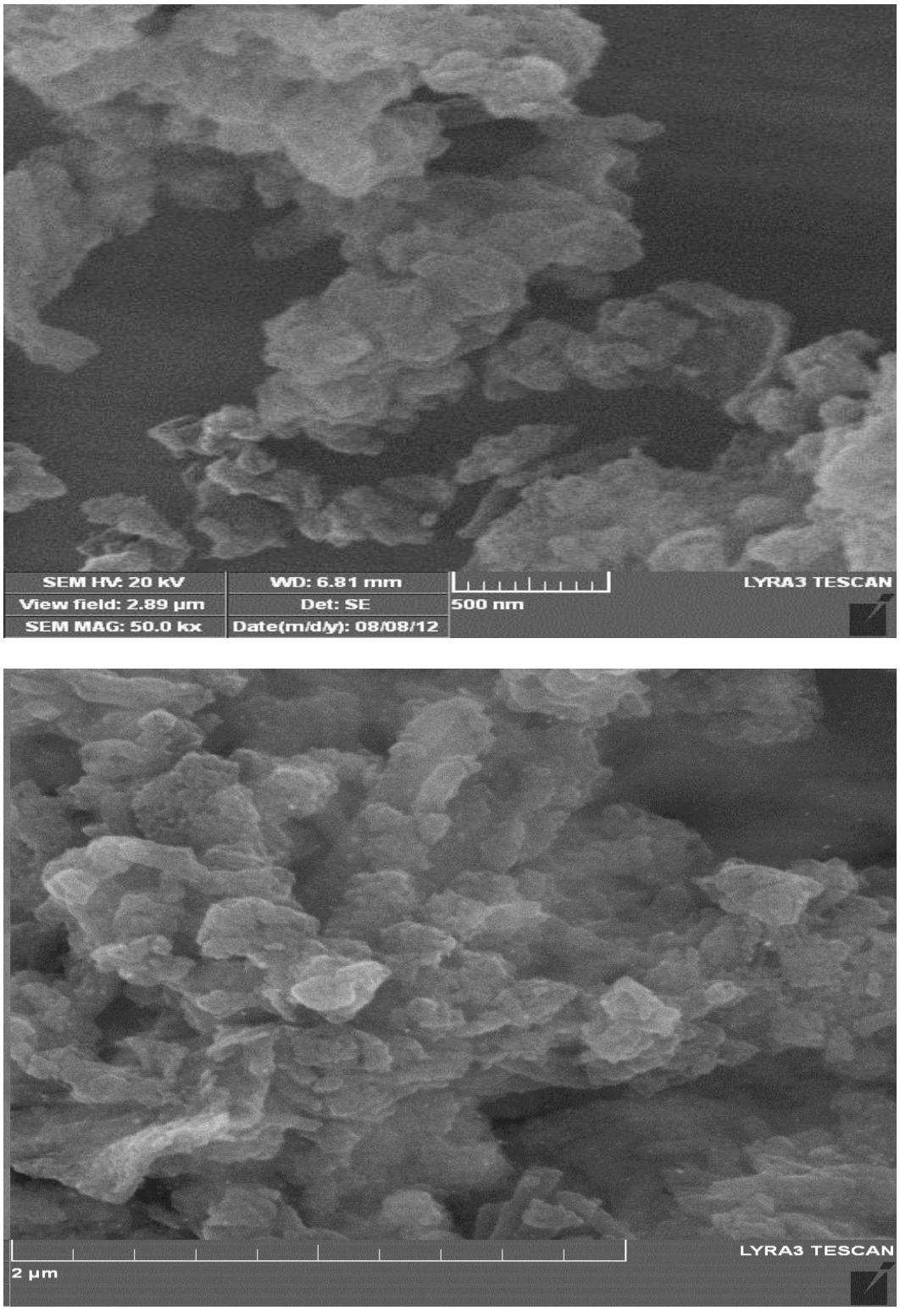


Figure 3-9 The FESEM image of RHA-Pt (a) 500nm and (b) 2µm

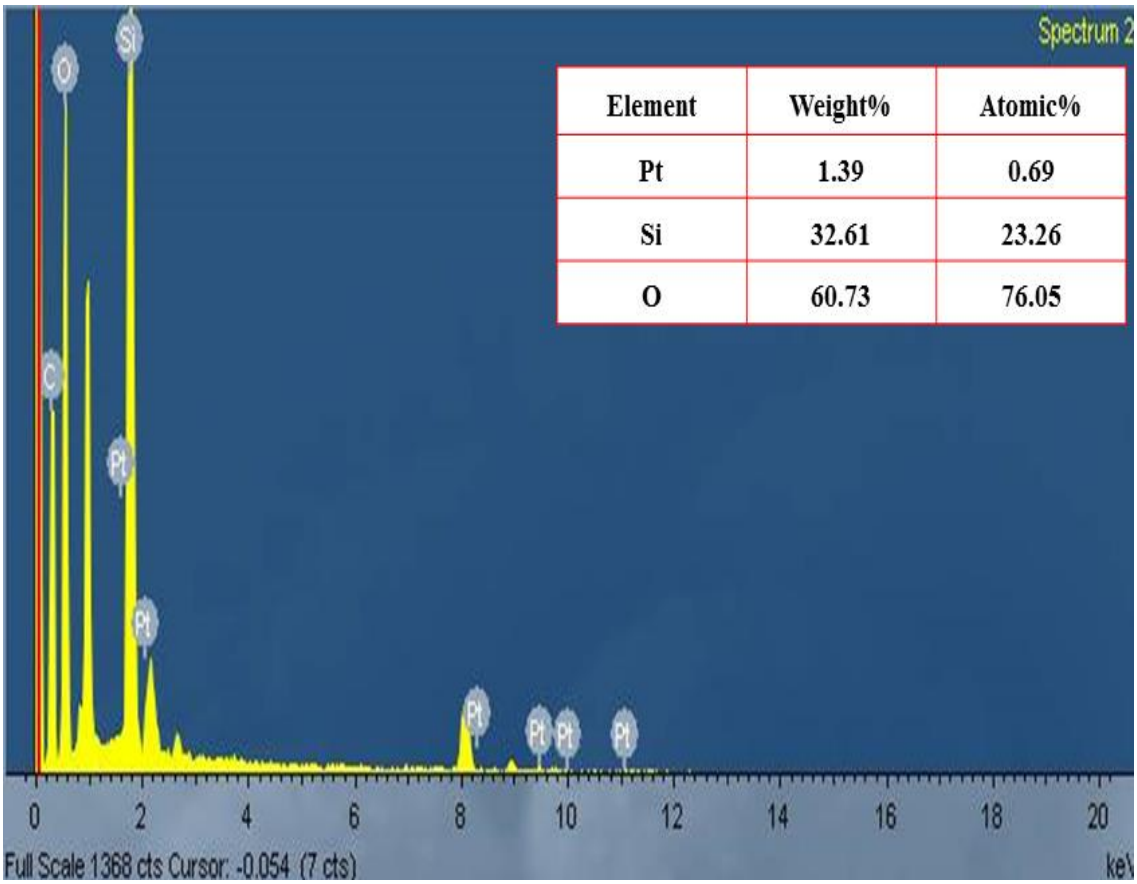


Figure 3-10 EDX spectrum of RHA-Pt. Inset is th percentages of the RHA-Pt component in the sample

3.4 Catalytic hydrodechlorination (HDC) by conventional method

HDC reactions of 8270 MagaMix with molecular hydrogen gas was carried out at room temperature and ambient pressure by using buffered solutions in a round bottom flask. Hydrogen was introduced by balloon (Fig. 11). In a typical HDC procedure, 100µL of 8270 MagaMix (100 PPM), 10 mL of buffer solution and 50 mg of supported Pt catalyst RHA-Pt (10% Pt), or 50 mg of RHA-Ti (10% Ti) was added [2]. The mixture magnetically stirred at (100 rpm) with a stirring bar and after the desired time (2hrs,16hrs,24hrs), the samples reaction mixture were collected, and separated by 1.5 mL Heptane solvent for 5min. The identification and quantification of all CBs and CPs were performed by GC–MS and Catalytic conversion was calculated by analyzing the peak areas of the target compounds. The set up is displayed in Fig. 11.The buffer solutions used in the HDC reactions were prepared as follows: (a) phosphate buffer: phosphoric-acid H_3PO_4 (2 mol L^{-1}) was added to a solution of K_2HPO_4 (2 mol L^{-1}) until the pH reaches 2, (b) phosphate buffer: a solution of NaH_2PO_4 (0.021 mol L^{-1}) was added to a solution of Na_2HPO_4 (0.029 mol L^{-1}) until the pH reaches 7, (c) borate buffer : a solution of sodium tetraborate (0.013 mol L^{-1}) was added to a solution of NaOH (0.018 mol L^{-1}) until the pH reaches 10.

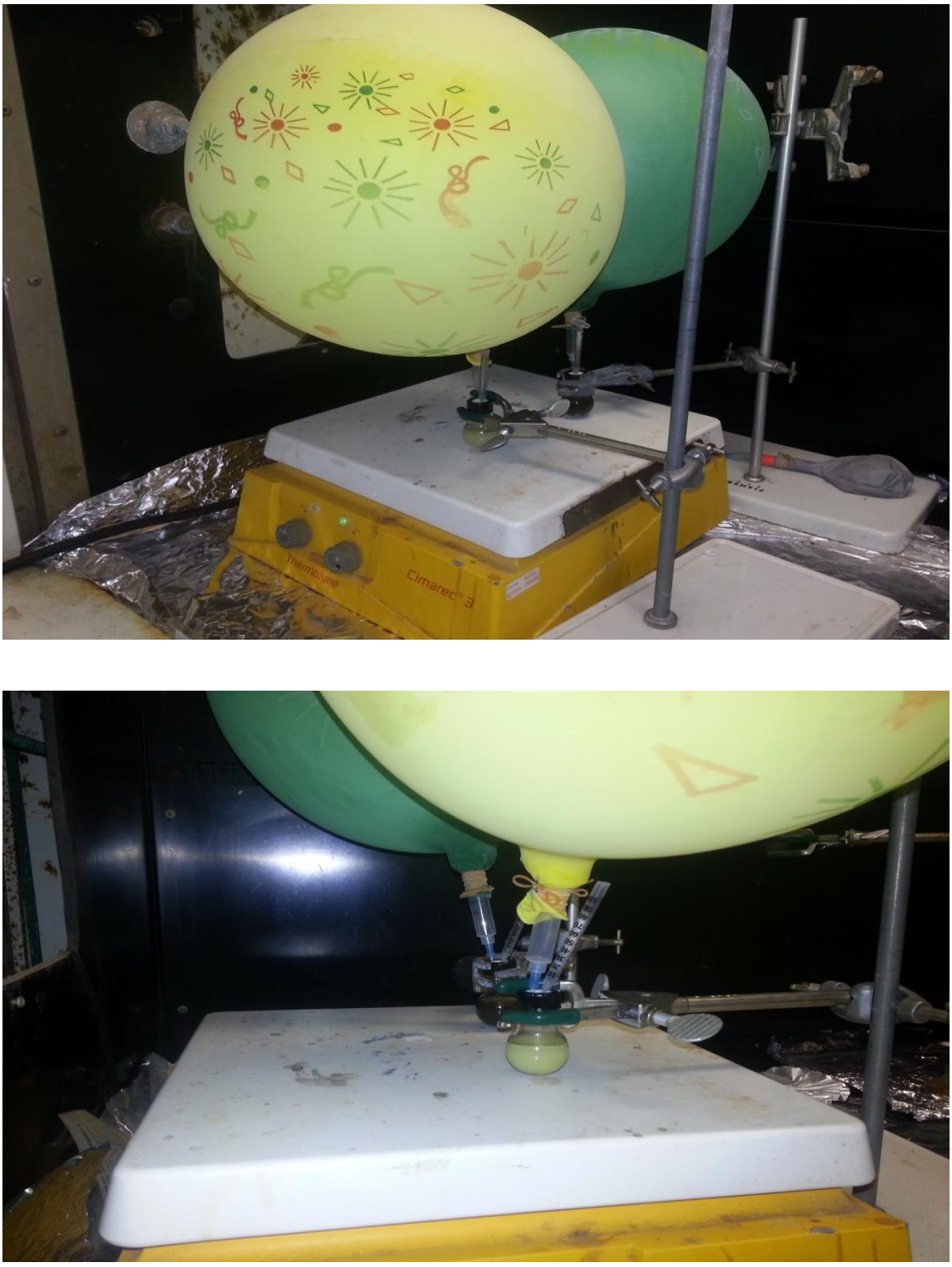


Figure 3-11 Schematics of the conventional method experimental setup for transfer hydrogeniysis reaction with external supplemented hydrogen gas source (H_2 in balloon)

3.5 HDC reaction in a capillary-microreactor

The capillary-microreactor was used for studying the detoxification of chlorinated organic compounds. Several glass capillary microreactores was designed for the HDC reaction as shown in Fig.12. The capillary-microreactor and reservoirs A and B were filled with 2.5 mmol of buffer solution of different pH (2,7and10) and 12.5 mg of Catalyst and 100 µL of the mixture standard (8270 MagaMix) were introduced into the capillary reactants at the reservoir A. Platinum wires was used as the electrodes and high voltage (1-5kV) applied. No Air bubbles were found inside the capillary tube during the reaction. A reaction potential of (1-5KV) and 200 µA current were applied to reservoir A. While reservoir B was connected to ground. HDC reaction was carried out at room temperature and ambient pressure, all experiments were repeated three times, to get more accurate results and the reaction time was controlled manually. The basic arrangement of the capillary-microreactor, in which the experimental studies for the detoxification of chlorinated organic compounds were carried out, is depicted in Fig. 13. The Setup of the capillary microreactor system is composed of a high voltage power supply, glass capillary microreactore and Platinum wires.

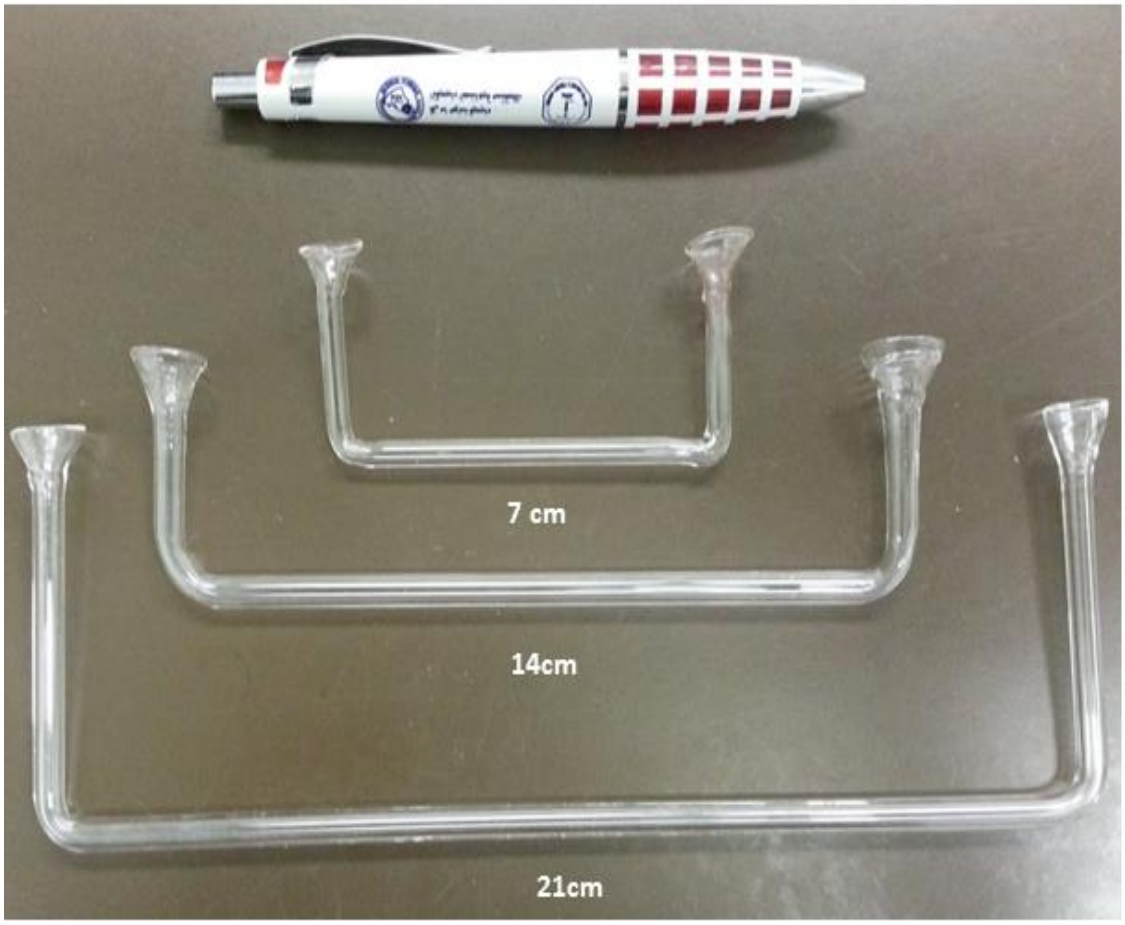


Figure 3-12 Glass capillary microreactores various lengths (7cm, 14cm, 21cm) which designed and used for the HDC reaction

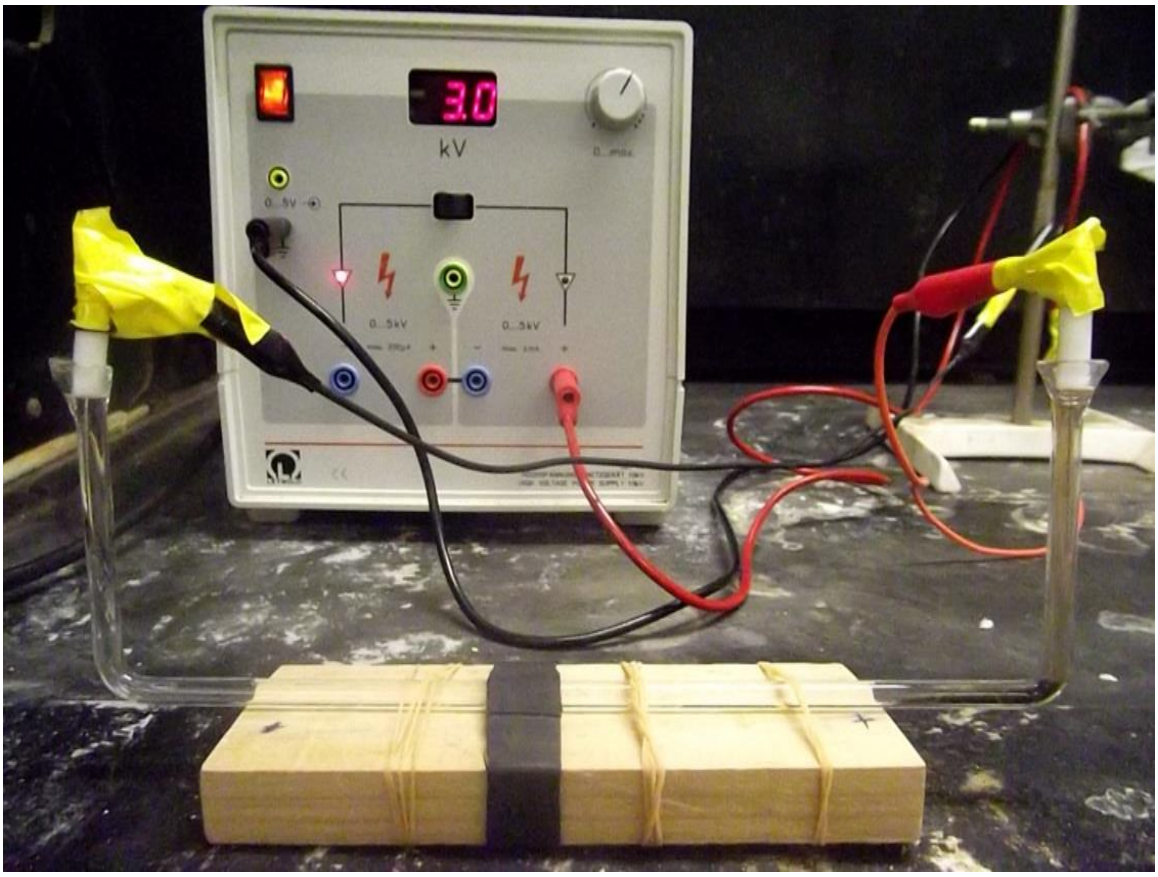
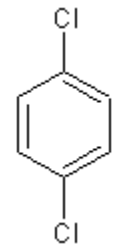


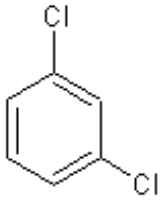
Figure 3-13 Experimental set-up of the capillary-microreactor system used for the detoxification of chlorinated organic compounds

3.6 Commonly found COCs in water: Target compounds

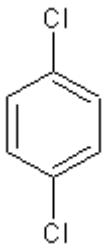
The target COCs that were detoxified are: chlorinated aromatic hydrocarbons include various chlorobenzenes and Chlorophenols, as 1,2-dichloroBenzene (1,2-DCB), 1,3-dichloro,Benzene (1,3-DCB), 1,4-dichloroBenzene (1,4-DCB), 1,2,4-trichloro Benzene (1,2,4-DCB), Hexachloro-Benzene (HCB), 2-chloroPhenol (2-CP), 2,4-dichloroPhenol (2,4-DCP), 2,4,5-trichloro-Phenol (2,4,5-TCP), 2,4,6-Trichlorophenol (2,4,6-TCP), 2,3,4,6 tetrachlorophenol (2,3,4,6-TeCP), 2,3,5,6-tetrachloroPhenol (2,3,5,6-TeCP), and pentachloro-Phenol(PCP). Chemical structures of COCs shown in Figure 14



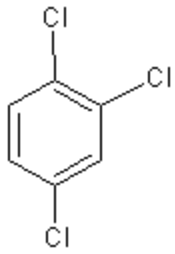
1,2- DCB



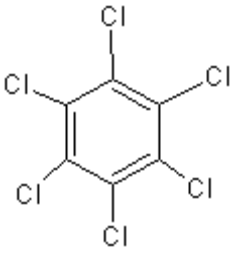
1,3-DCB



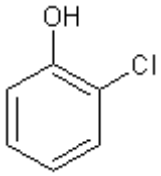
1,4-DCB



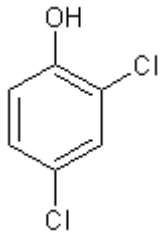
1,2,4-TCB



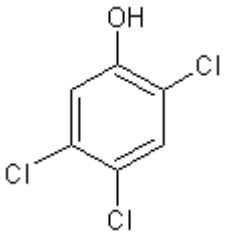
HCB



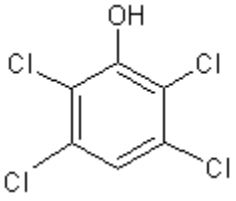
2-CP



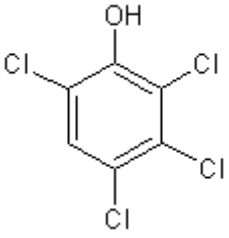
2,4-DCP



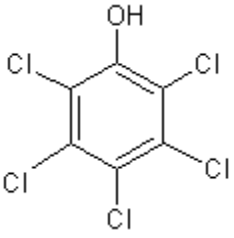
2,4,5-TCP



2,3,5,6-TeCP



2,3,4,6-TeCP



PCP

Figure 3-14 chemical structures of target chlorinated organic compounds COCs

3.7 Instrumental Analysis Condition

Analyses were carried out using a gas chromatograph (Agilent technologies, 6890N GC) with autosampler 7683B series and a 6890B injector coupled with a mass spectrometer (Agilent technologies, 5975B MSD). An Agilent 19091Z-213 column of 30m x 0.32mm dimensions(ID) and a film thickness of 1µm HP-1 methyl siloxane stationary phase were used. High purity helium (>99.999%) flowing at a rate of 2.0ml min^{-1} was used as carrier gas and the samples were analyzed in a constant flow at 1.2 mL min^{-1}. The oven temperature program used for the analyses was as follows: the initial temperature was 55 ºC held 15 min which was then increased to 250 ºC at 6 ºC min-1 and held for 2 min. Samples were injected in splitless mode, interface and detector temperatures were all set at 250oC. These conditions are Summarize in Table 2. The total GC analysis time was 77 minutes. For qualitative determinations, the MSD was operated in full-scan mode from m/z 50 to 550. For quantitative determinations, the MSD was operated in selected ion monitoring (SIM) mode.

Table 3-2 Gas Chromatographic conditions for the determination of COCs

Instrument	Agilent, 6890N system
Column	19091Z-213 capillary column of 30m x320µm x1µm, HP-1 methyl siloxane
He flow rate	1.2 ml min-1
Injection mode	splitless
Injection volume	1µl
Injection port temperature	250°C
Oven temperature program	55°C (15 min) ramped at 6°C/min to 250°C (30 min)
MS Detector temperature	250°C
Interface temperature	250°C
Acquisition mode	SCAN (50-550)/SIM

CHAPTER 4

RESULTS & DISCUSSIONS

4.1 PART 1: Detoxification of COCs using conventional method

Table 1-3 summarize the conversions obtained in the catalytic HDC of chlorobenzenes and Chlorophenols in different time and different buffer solutions with RHA-Pt and RHA-Ti catalysts. All experiments were repeated two to three times, to get more accurate results and the reaction time was controlled manually. Fig (1-6) show the effect of pH on HDC of (CBs and CPs) in different buffer solutions and catalysts, when aqueous buffer solutions were used, the HCl formed during the HDC reaction was neutralized. Buffer of pH (7 and 10) increased the conversion (%) of (CBs and CPs) to benzene more than the pH 2 over RHA-Ti catalyst, whereas the degradation of (CBs and CPs) increased by using the pH (2 and 7) more than pH 10 over RHA-Pt catalyst. That may be due to the dissolve of platinum particles in the basic medium [28]. Fig (7-12) show Influence of reaction times on the degradation of (CBs and CPs) in different buffer solutions and catalysts, the Conversion (%) increases with increase in reaction time from 2HR to 24HR, which appears to be an optimum period With complete conversion (~100%).

Table 4-1The Effect of different reaction times on the conversion ratio by the conventional method by using phosphate buffer of pH 2 and RHA-Pt and RHA-Ti catalysts

Catalyst	RHA-Pt			RHA-Ti		
Compound name	2HR	16HR	24HR	2HR	16HR	24HR
1,2-DCB	44	100	100	18	98	100
1,3-DCB	43	95	99	10	90	98
1,4-DCB	44	100	100	20	91	97
1,2,4-TCB	40	100	100	15	100	100
HCB	35	90	94	19	82	100
2CP	44	100	100	37	71	100
2,4-DCP	38	92	94	29	77	93
2,4,5-TCP	35	80	93	18	74	100
2,4,6-TCP	37	100	95	23	63	100
2,3,4,6-TeCP	35	77	90	29	81	100
2,3,5,6-TeCP	30	80	95	30	70	100
PCP	28	95	96	37	68	81

Table 4-2 The Effect of different reaction times on the conversion ratio by the conventional method by using phosphate buffer of pH 7 and RHA-Pt and RHA-Ti catalysts

Catalyst	RHA-Pt			RHA-Ti		
Compound name	2HR	16HR	24HR	2HR	16HR	24HR
1,2-DCB	41	97	100	44	95	100
1,3-DCB	38	95	95	36	94	96
1,4-DCB	40	95	100	45	95	100
1,2,4-TCB	37	96	98	40	95	98
HCB	33	94	96	35	100	96
2CP	40	100	100	42	80	94
2,4-DCP	36	96	100	38	88	92
2,4,5-TCP	33	100	95	36	79	91
2,4,6-TCP	32	94	92	44	87	89
2,3,4,6-TeCP	26	92	91	40	100	100
2,3,5,6-TeCP	25	94	90	45	100	92
PCP	24	100	90	46	84	89

Table 4-3 The Effect of different reaction times on the conversion ratio by the conventional method by using phosphate buffer of pH 10 and RHA-Pt and RHA-Ti catalyst

Catalyst	RHA-Pt			RHA-Ti		
Compound name	2HR	16HR	24HR	2HR	16HR	24HR
1,2- DCB	38	95	99	56	97	97
1,3- DCB	29	92	96	52	91	95
1,4- DCB	35	93	97	50	95	100
1,2,4 TCB	28	90	96	48	100	99
HCB	25	87	92	42	88	95
2CP	32	84	94	57	88	88
2,4- DCP	31	68	100	48	85	100
2,4,5- TCP	25	82	100	45	95	93
2,4,6- TCP	27	86	96	42	100	93
2,3,4,6 -TeCP	22	79	97	44	100	100
2,3,5,6 TeCP	20	90	95	50	100	100
PCP	20	74	100	40	80	85

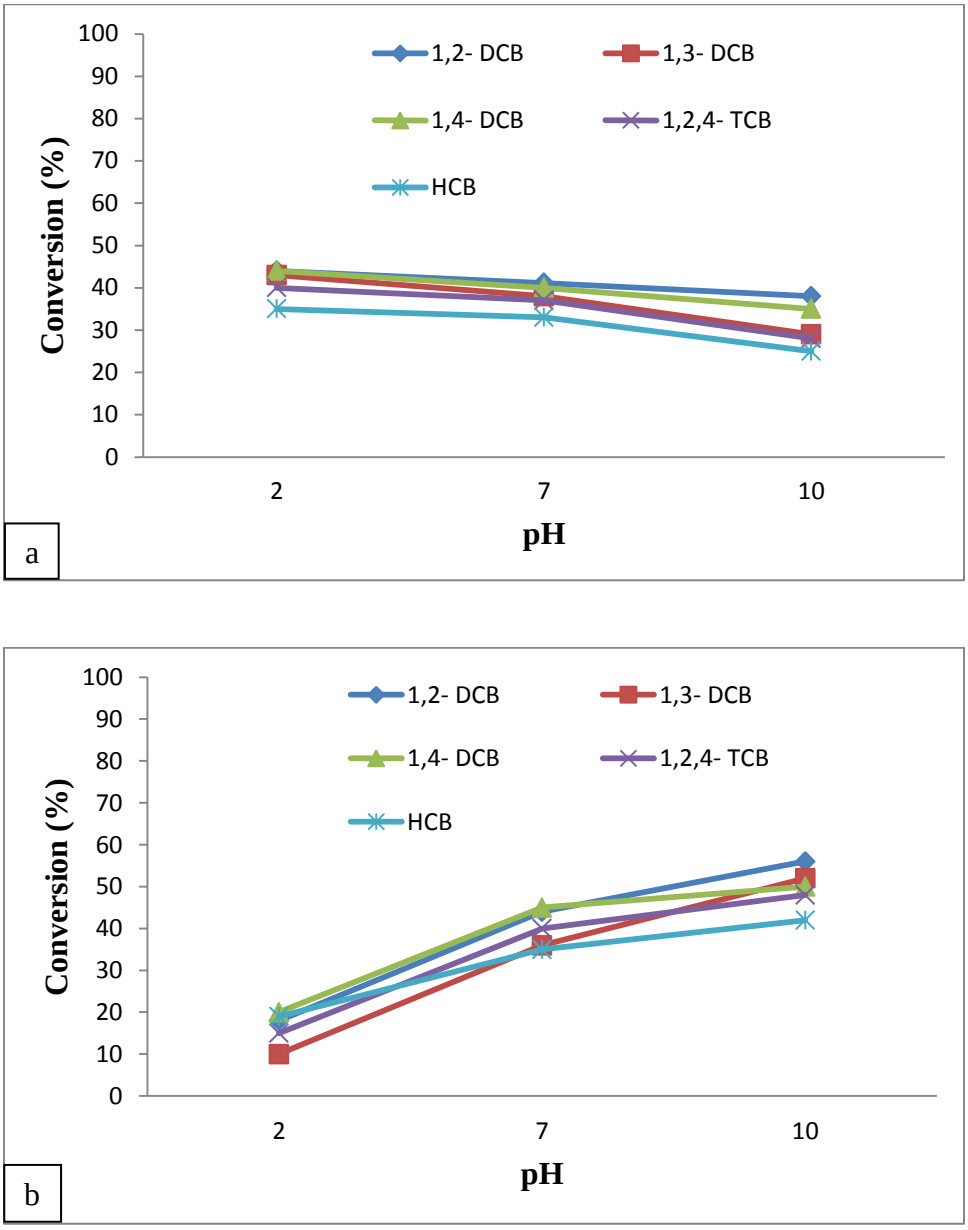


Figure 4-1 The Effect of reaction pH on the conversion ratio of chlorobenzenes (CBs) by the conventional method (after 2HR) by using (a) RHA-Pt and (b) RHA-Ti

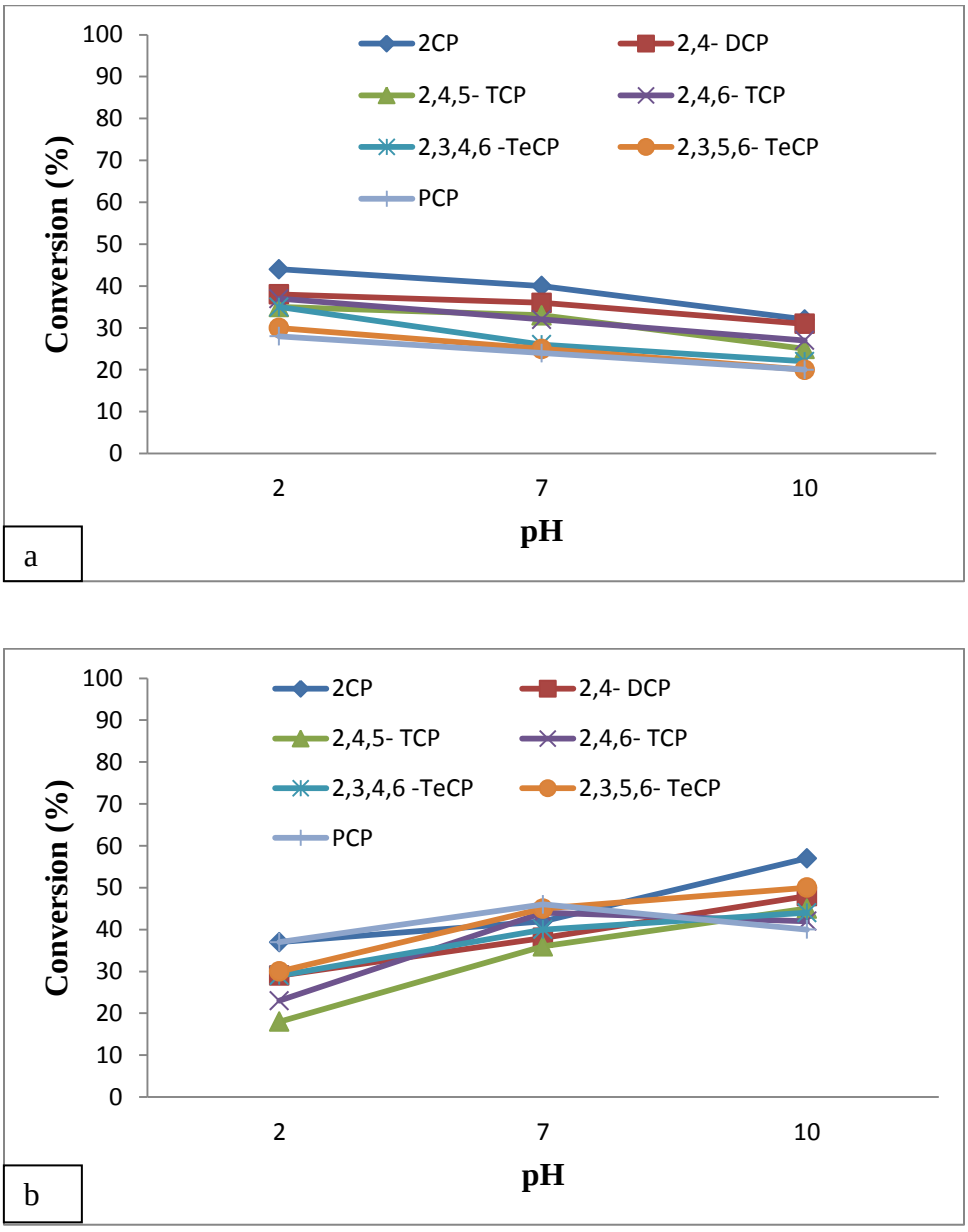


Figure 4-2 The Effect of reaction pH on the conversion ratio of Chlorophenols (CPs) by the conventional method (after 2HR) by using (a) RHA-Pt and (b) RHA-Ti

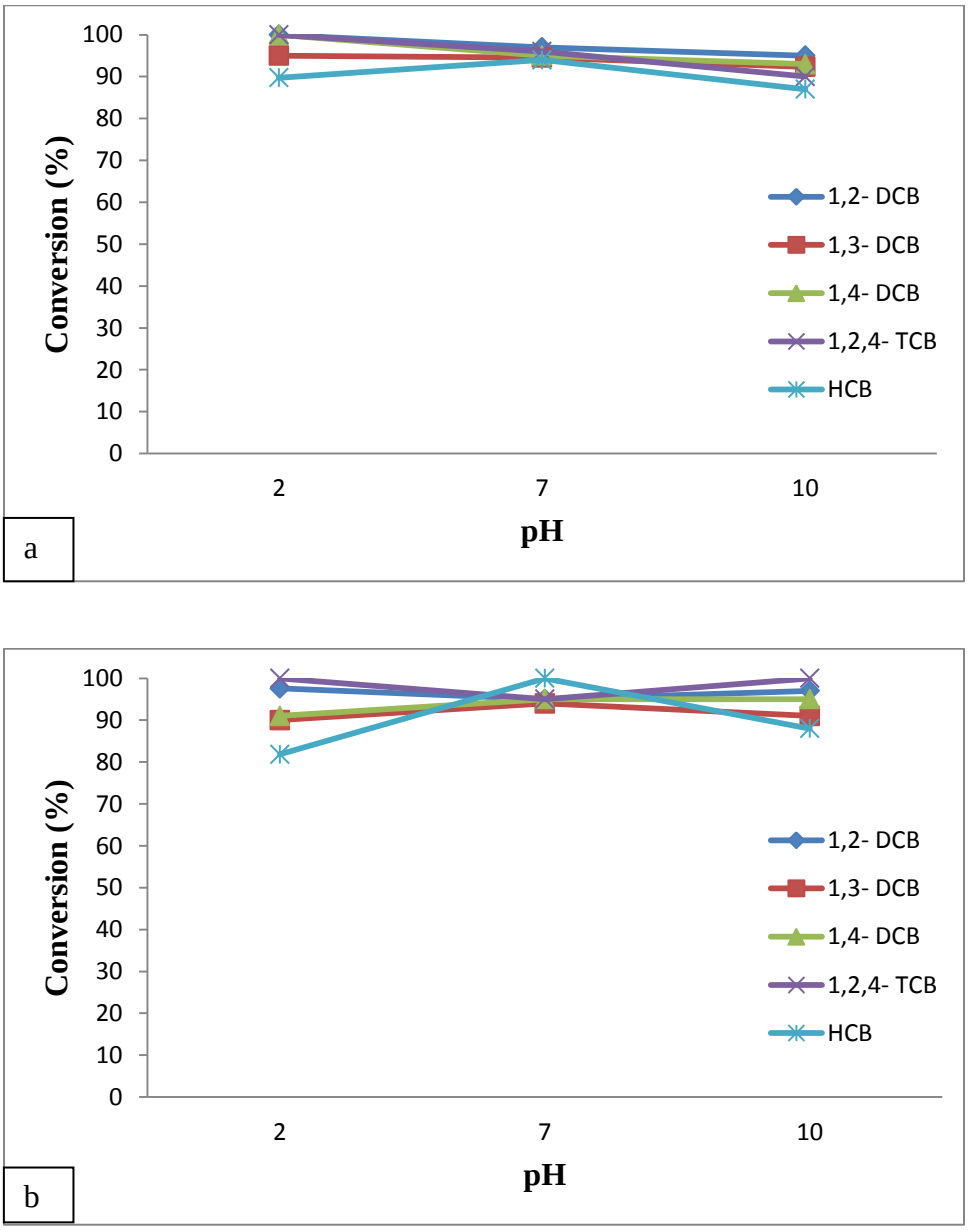


Figure 4-3 The Effect of reaction pH on the conversion ratio of chlorobenzenes (CBs) by the conventional method (after 16HR) by using (a) RHA-Pt and (b) RHA-Ti

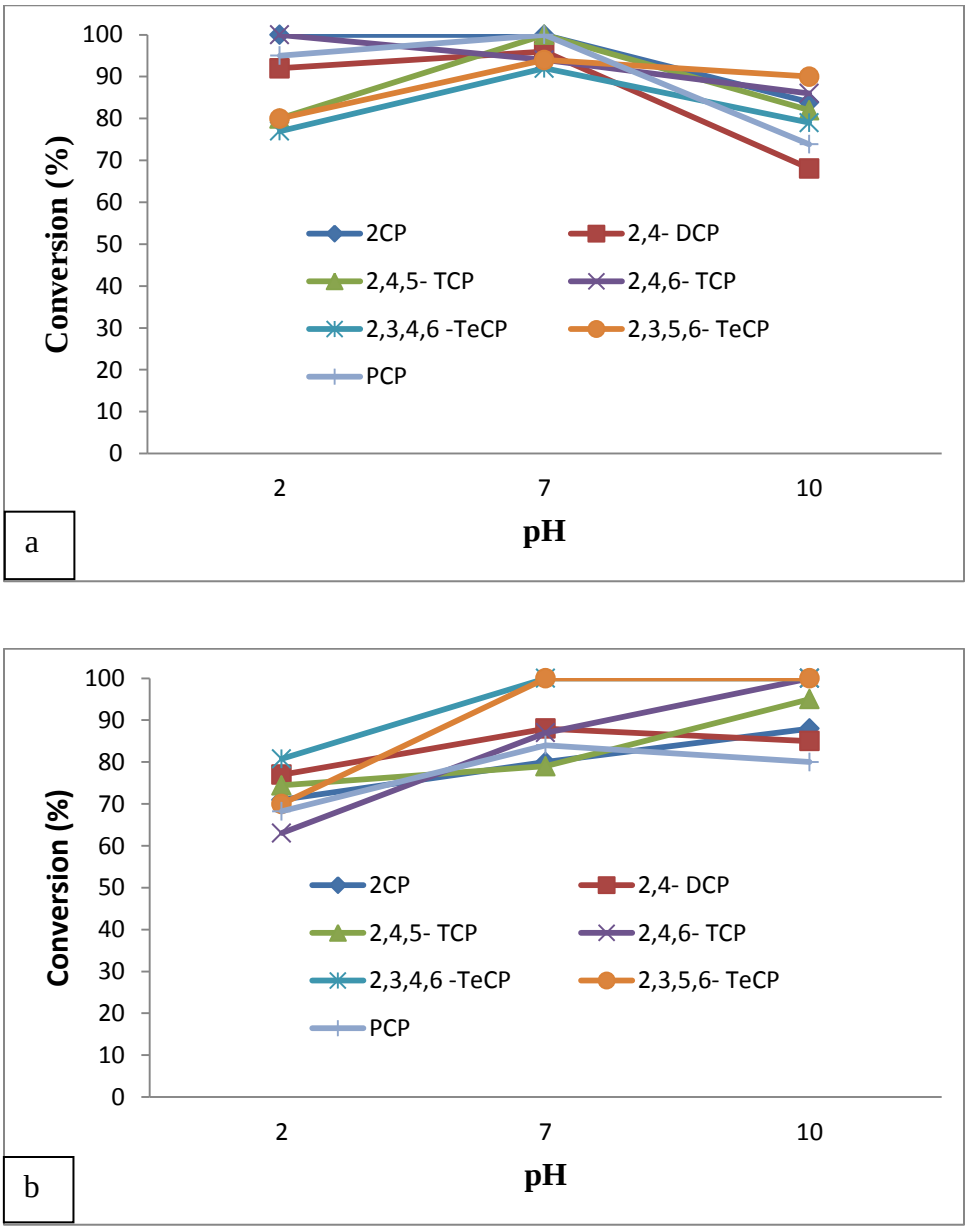


Figure 4-4 The Effect of reaction pH on the conversion ratio of Chlorophenols (CPs) by the conventional method (after 16HR) by using (a) RHA-Pt and (b) RHA-Ti

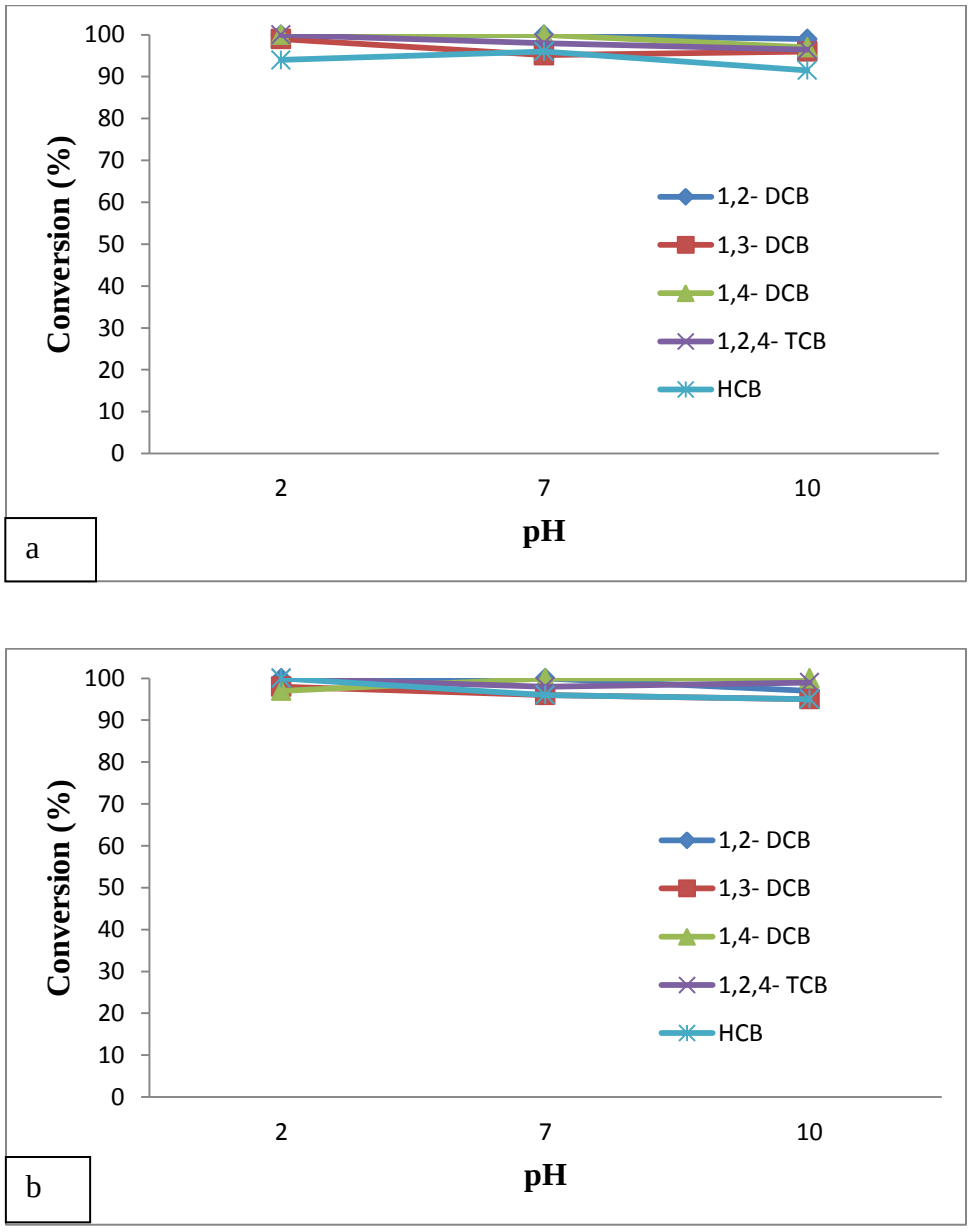


Figure 4-5 The Effect of reaction pH on the conversion ratio of chlorobenzenes (CBs) by the conventional method (after 24HR) by using (a) RHA-Pt and (b) RHA-Ti

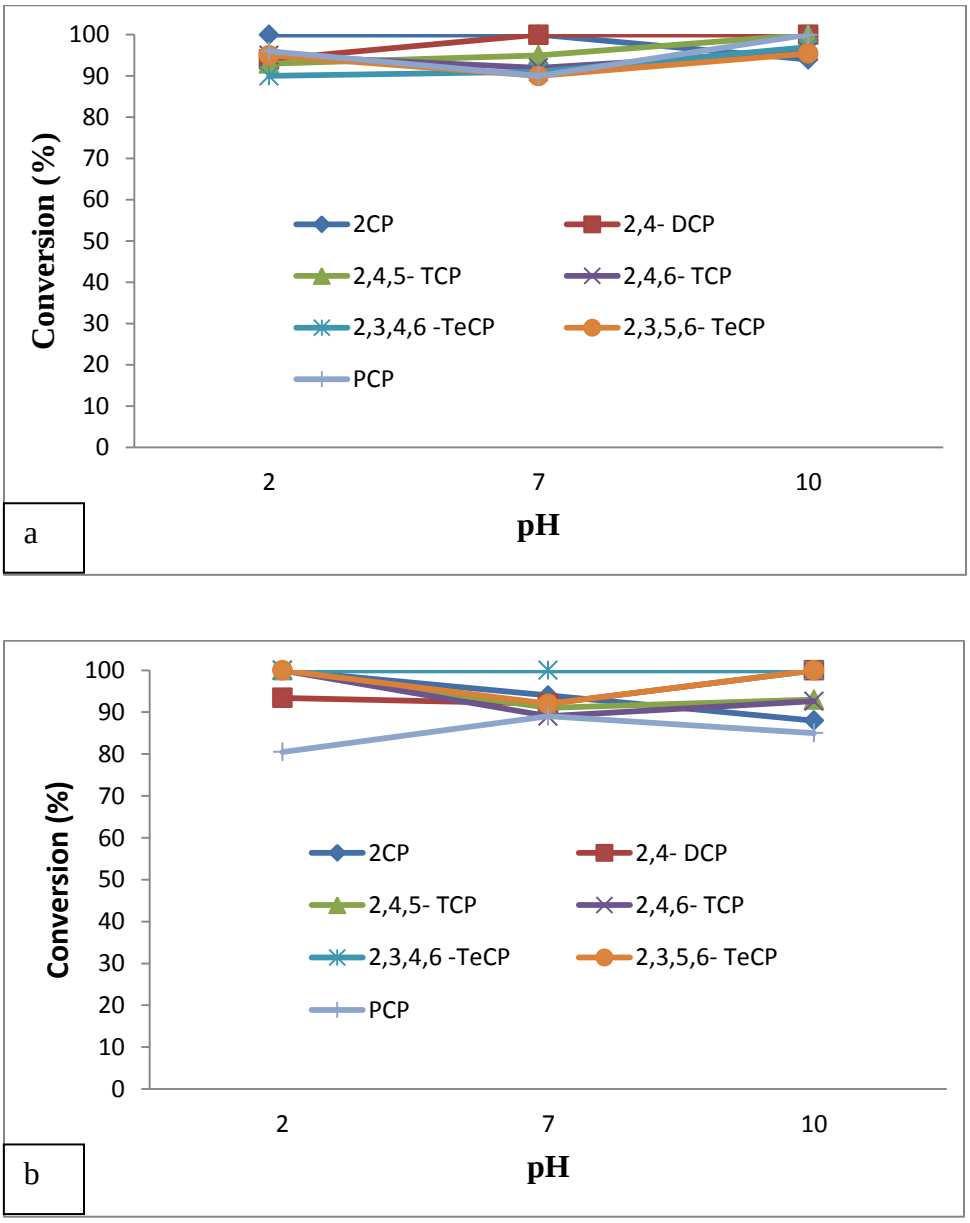


Figure 4-6 The Effect of reaction pH on the conversion ratio of Chlorophenols (CPs) by the conventional method (after 24HR) by using (a) RHA-Pt and (b) RHA-Ti

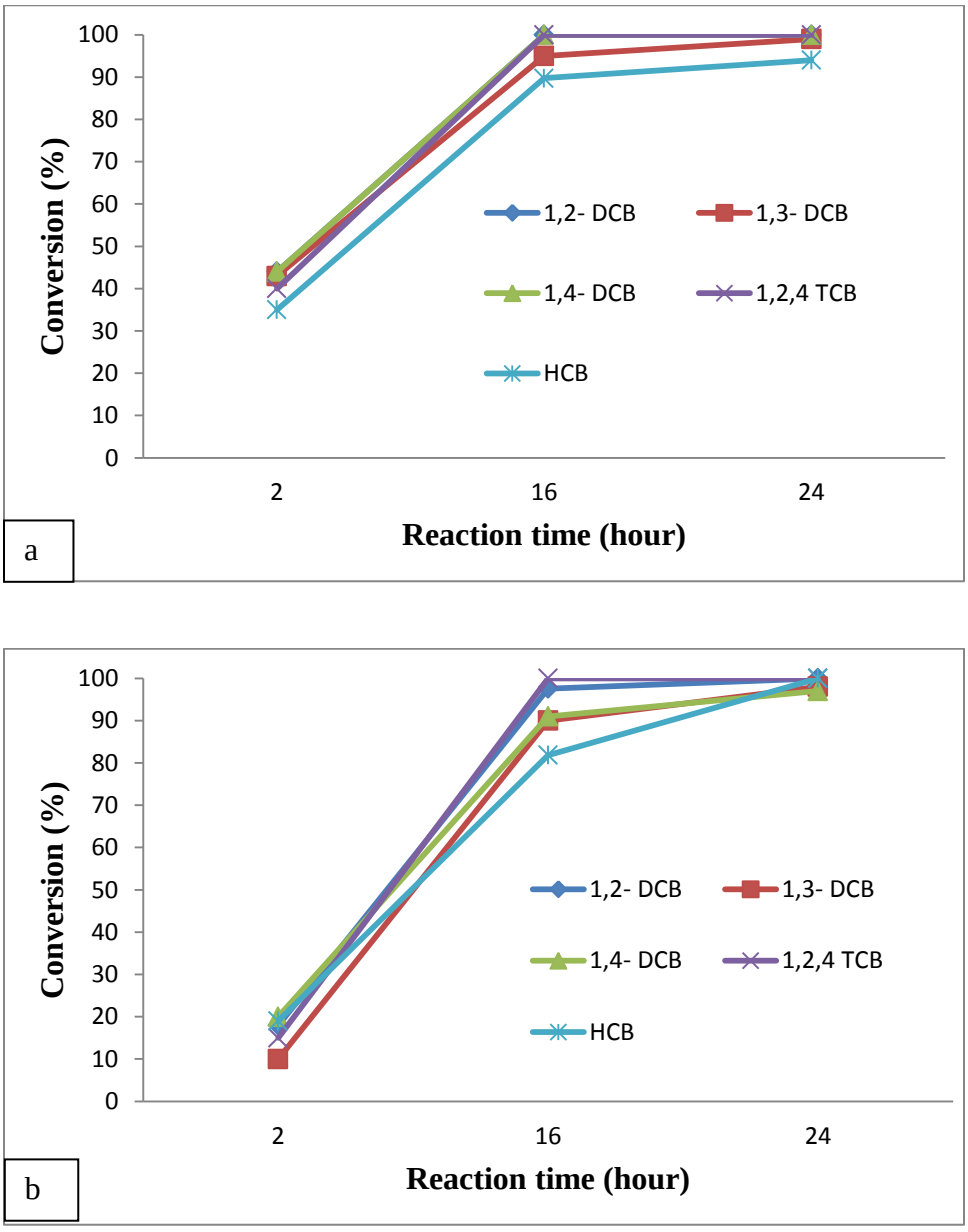


Figure 4-7 The Effect of different reaction time on the conversion ratio of chlorobenzenes (CBs) by the conventional method at pH 2 by using (a) RHA-Pt and (b) RHA-Ti

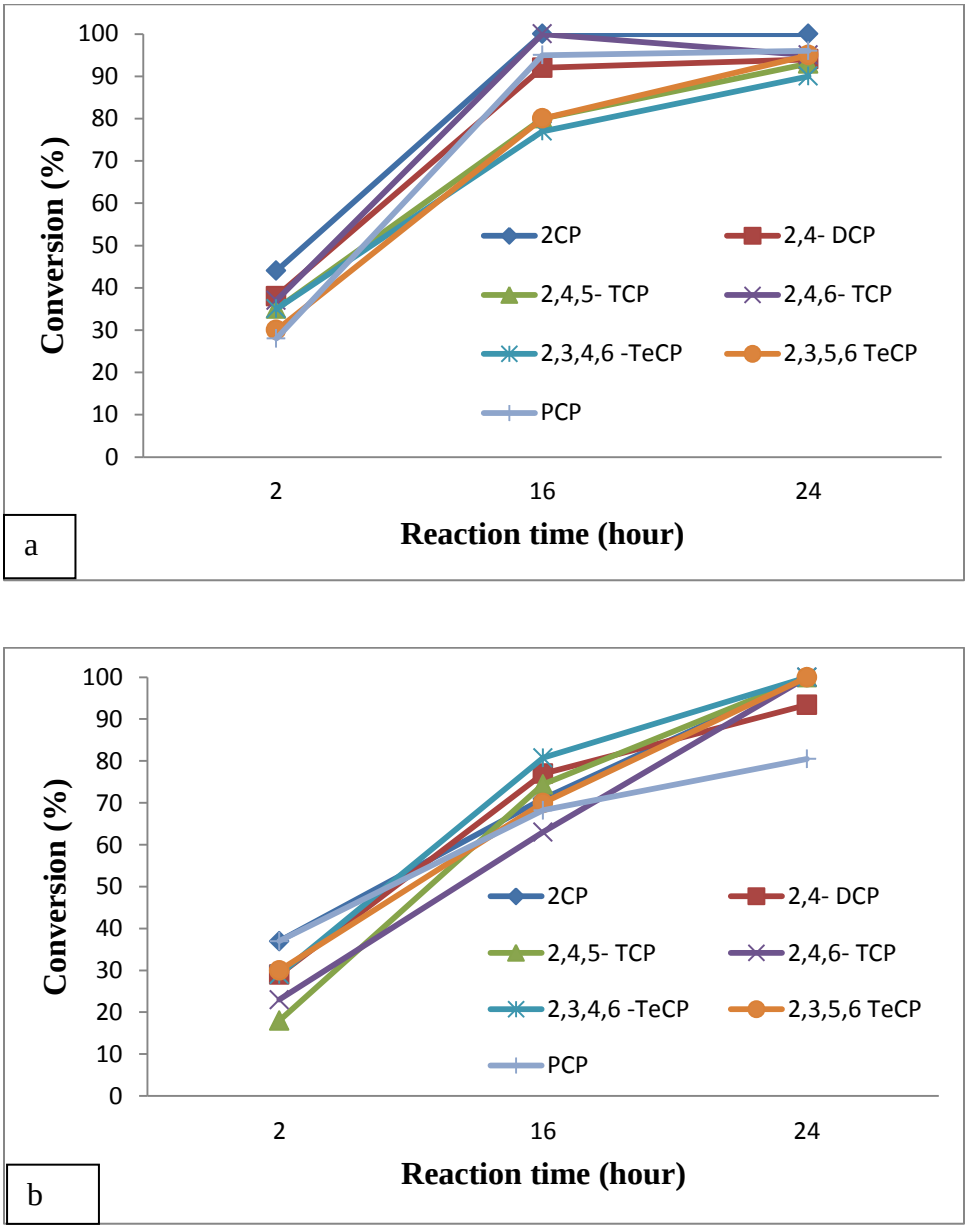


Figure 4-8 The Effect of different reaction time on the conversion ratio of Chlorophenols (CPs) by the conventional method at pH 2 by using (a) RHA-Pt and (b) RHA-Ti

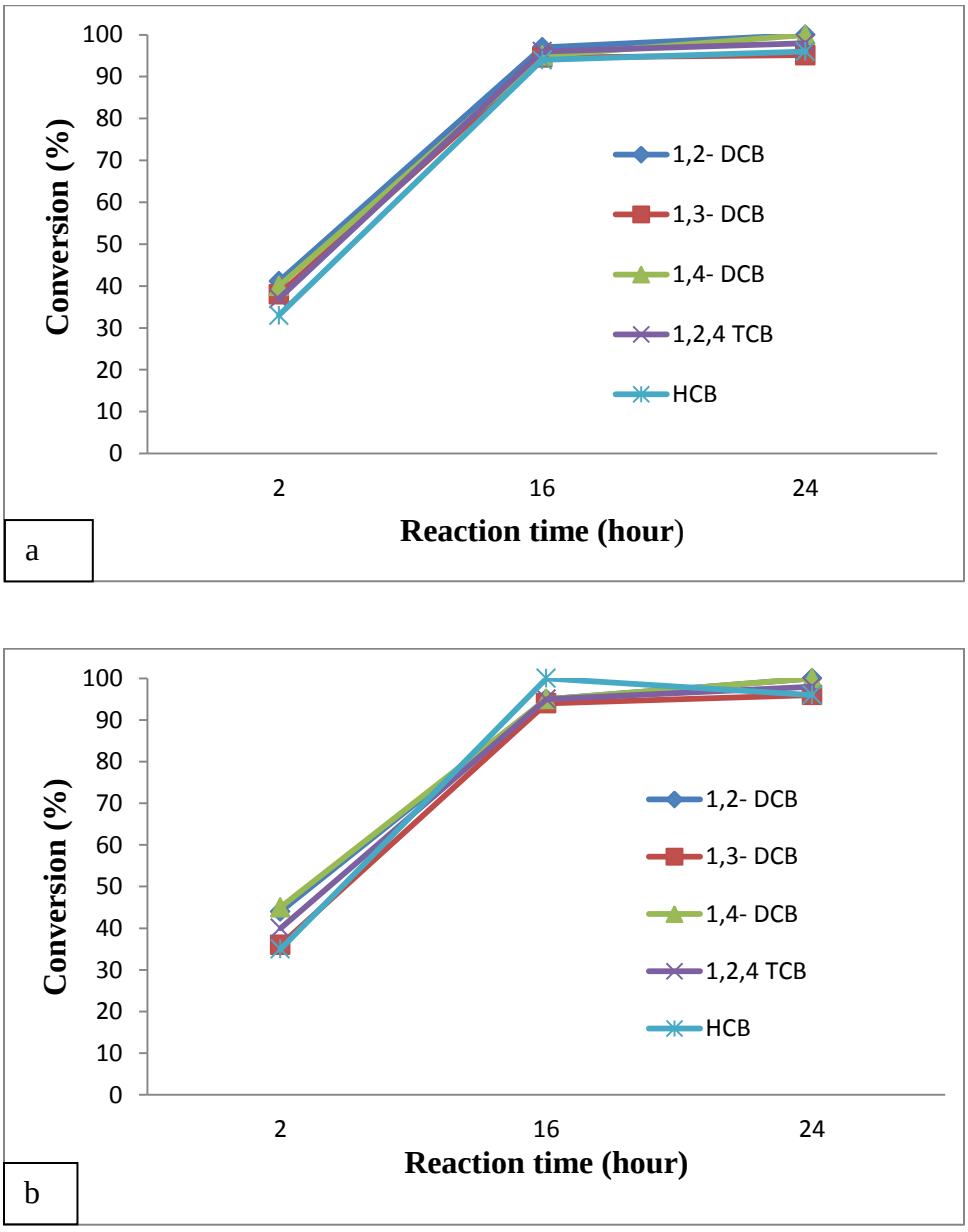


Figure 4-9 The Effect of different reaction time on the conversion ratio of chlorobenzenes (CBs) by the conventional method at pH 7 by using (a) RHA-Pt and (b) RHA-Ti

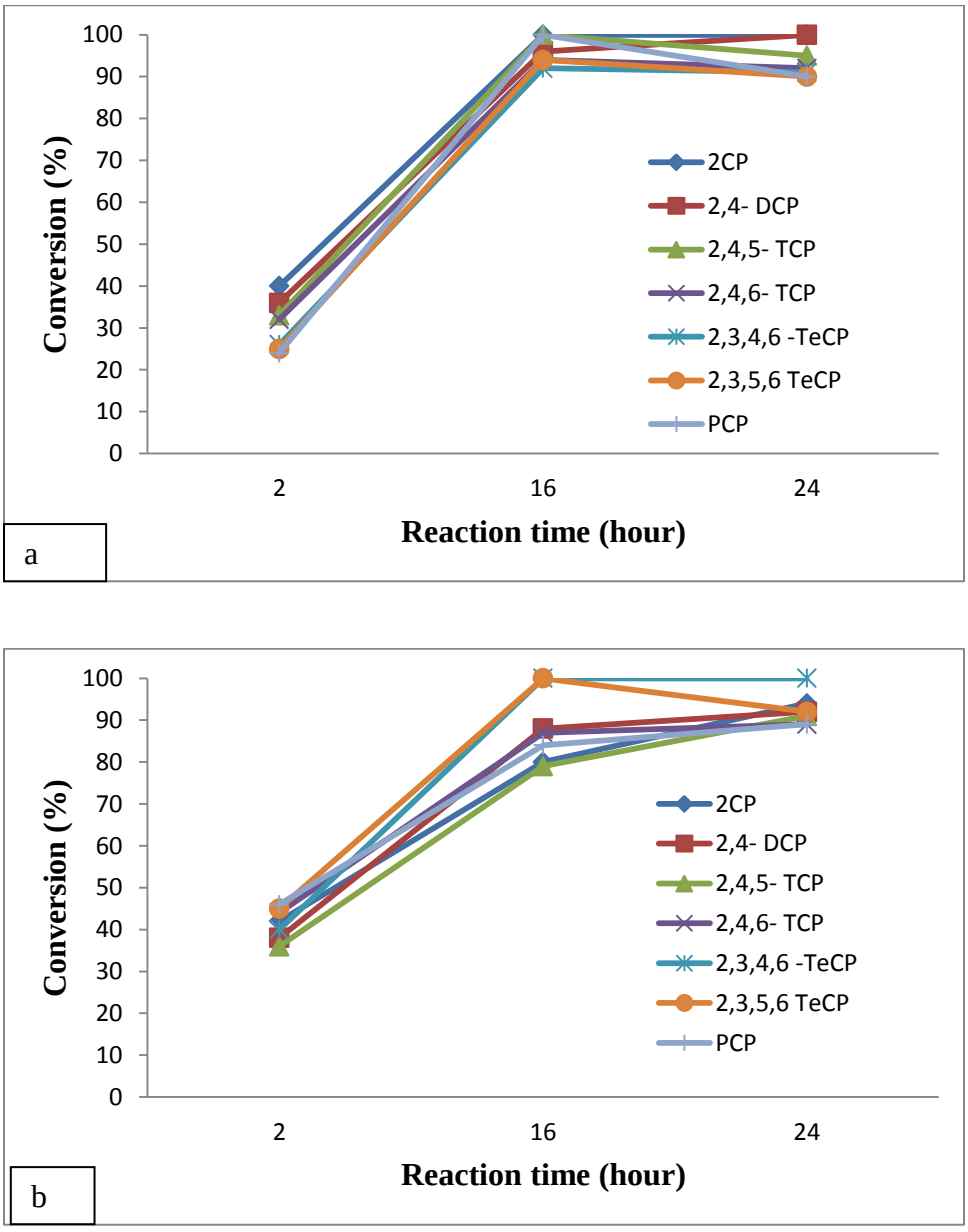


Figure 4-10 The Effect of different reaction time on the conversion ratio of Chlorophenols (CPs) by the conventional method at pH 7 by using (a) RHA-Pt and (b) RHA-Ti

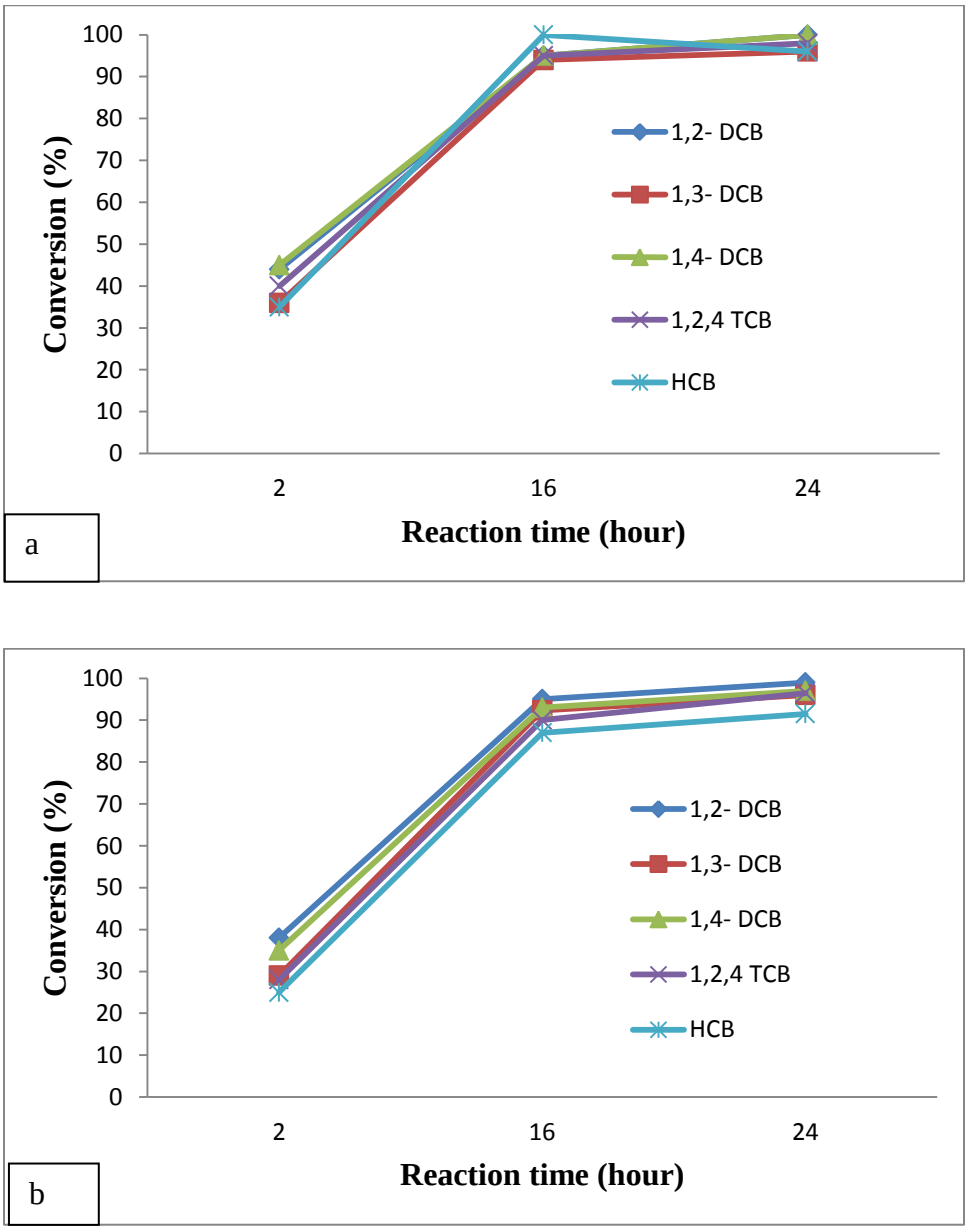


Figure 4-11 The Effect of different reaction time on the conversion ratio of chlorobenzenes (CBs) by the conventional method at pH 10 by using (a) RHA-Pt and (b) RHA-Ti

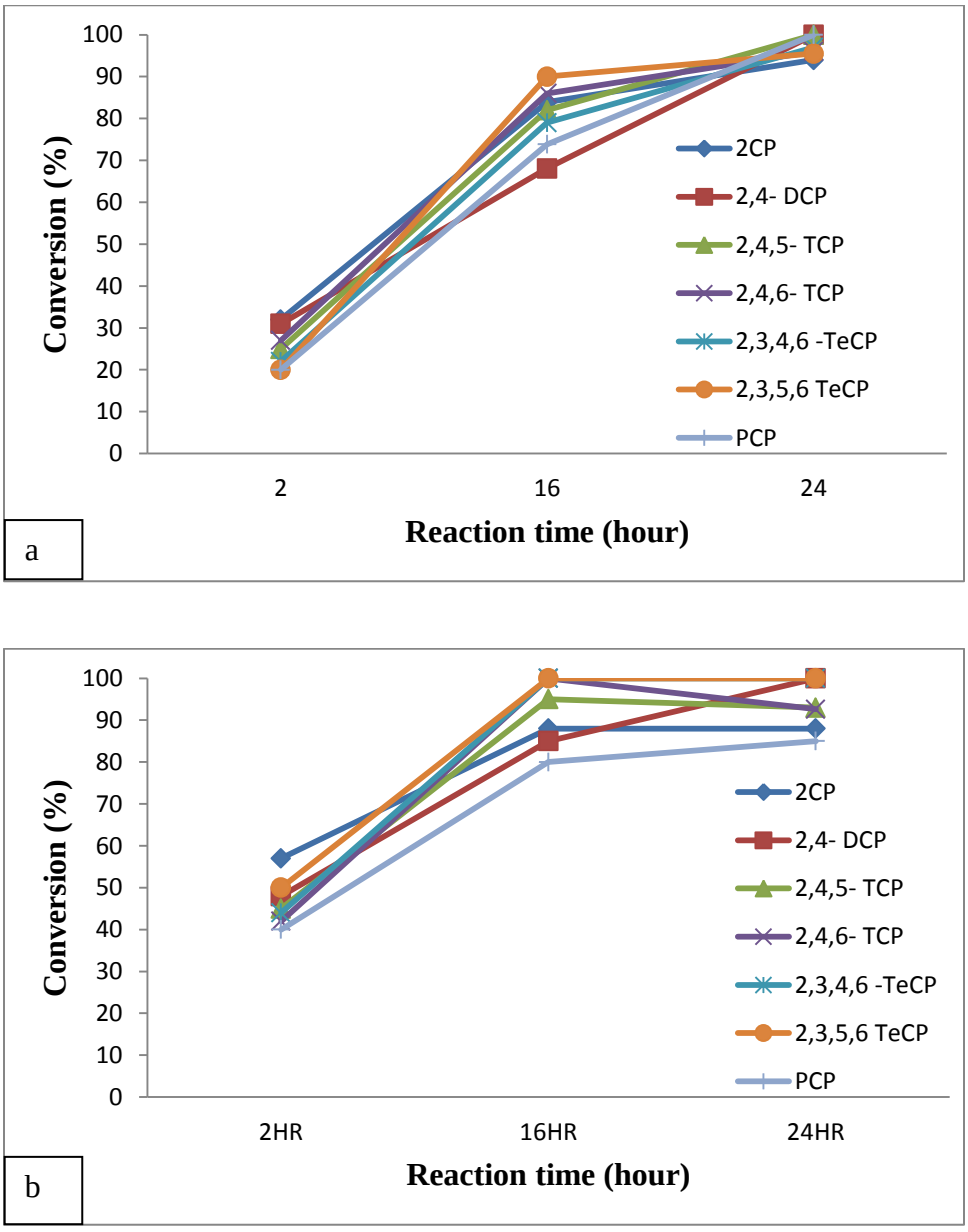


Figure 4-12 The Effect of different reaction time on the conversion ratio of Chlorophenols (CPs) by the conventional method at pH 10 by using (a) RHA-Pt and (b) RHA-Ti

4.2 PART 2: Detoxification of COCs using capillary microreactor

4.2.1 Optimization of capillary microreactor method for the HDC reaction

To optimize the HDC reactions in the capillary-microreactor, analytical factors like applied potential, reaction time, length of the capillary and pH of buffer solution was investigated to determine the most favorable reaction conditions. Temperature was kept at room temperature throughout the reactions. All experiments were repeated two to three times, to get more accurate results. The reaction time was controlled manually. The results were then compared with those of the conventional method. The identification and quantitative yields were determined which were obtained from (GC–MS) data.

4.2.2 Applied potential

In order to achieve a high detoxification of COCs different potential applied in the range of 1–5 kV at a constant current of 200 μA. Table 4 and 5 summarize the conversion(%) obtained in the catalytic HDC of chlorobenzenes and Chlorophenols in different time and different buffer solutions with RHA-Pt and RHA-Ti catalysts by applied different potential. Figures 13 and 14 show the influence of the applied potential on the HDC reactions. As can be seen, a maximum detoxification of COCs by both catalysts (RHA-Pt and RHA-Ti) was obtained by using 3kV. In a glass capillary microreactor high potential (in Kv range) was applied to create in-situ generation of hydrogen as well as to expedite the activation of catalysts for the detoxification of chlorobenzene and Chlorophenols. Moreover, the higher applied potential increases the analyte interaction with the catalyst

particles and enhances the hydrodechlorination (HDC) reaction to the detoxify of chlorobenzene and Chlorophenols [40,41].

Table 4-4 Effect of different applied potentials on the conversion ratio in the capillary-microreactor (at reaction time 20min and pH10 by using RHA-Pt

Compound name	Applied potential				
	1KV	2KV	3KV	4KV	5KV
1,2- DCB	94	96	98	97	96
1,3-DCB	67	82	90	81	73
1,4-DCB	93	96	97	95	92
1,2,4-TCB	91	94	94	89	89
HCB	87	90	94	85	83
2CP	51	72	90	85	80
2,4-DCP	42	81	85	85	79
2,4,5-TCP	89	90	96	95	90
2,4,6-TCP	89	92	99	97	100
2,3,4,6-TeCP	38	77	81	85	83
2,3,5,6-TeCP	40	80	85	88	80
PCP	55	74	85	80	80

Table 4-5 Effect of different applied potentials on the conversion ratio in the capillary-microreactor (at reaction time 10 and pH 10 by using RHA-Ti).

Compound name	Applied potential				
	1KV	2KV	3KV	4KV	5KV
1,2-DCB	63	75	85	82	80
1,3-DCB	53	78	80	81	75
1,4-DCB	59	82	91	92	81
1,2,4-TCB	38	70	87	85	81
HCB	41	81	89	88	85
2CP	31	87	75	80	77
2,4-DCP	43	86	91	95	100
2,4,5-TCP	39	80	96	95	98
2,4,6-TCP	30	83	100	100	100
2,3,4,6-TeCP	35	67	85	83	85
2,3,5,6-TeCP	36	75	76	80	75
PCP	57	66	76	74	72

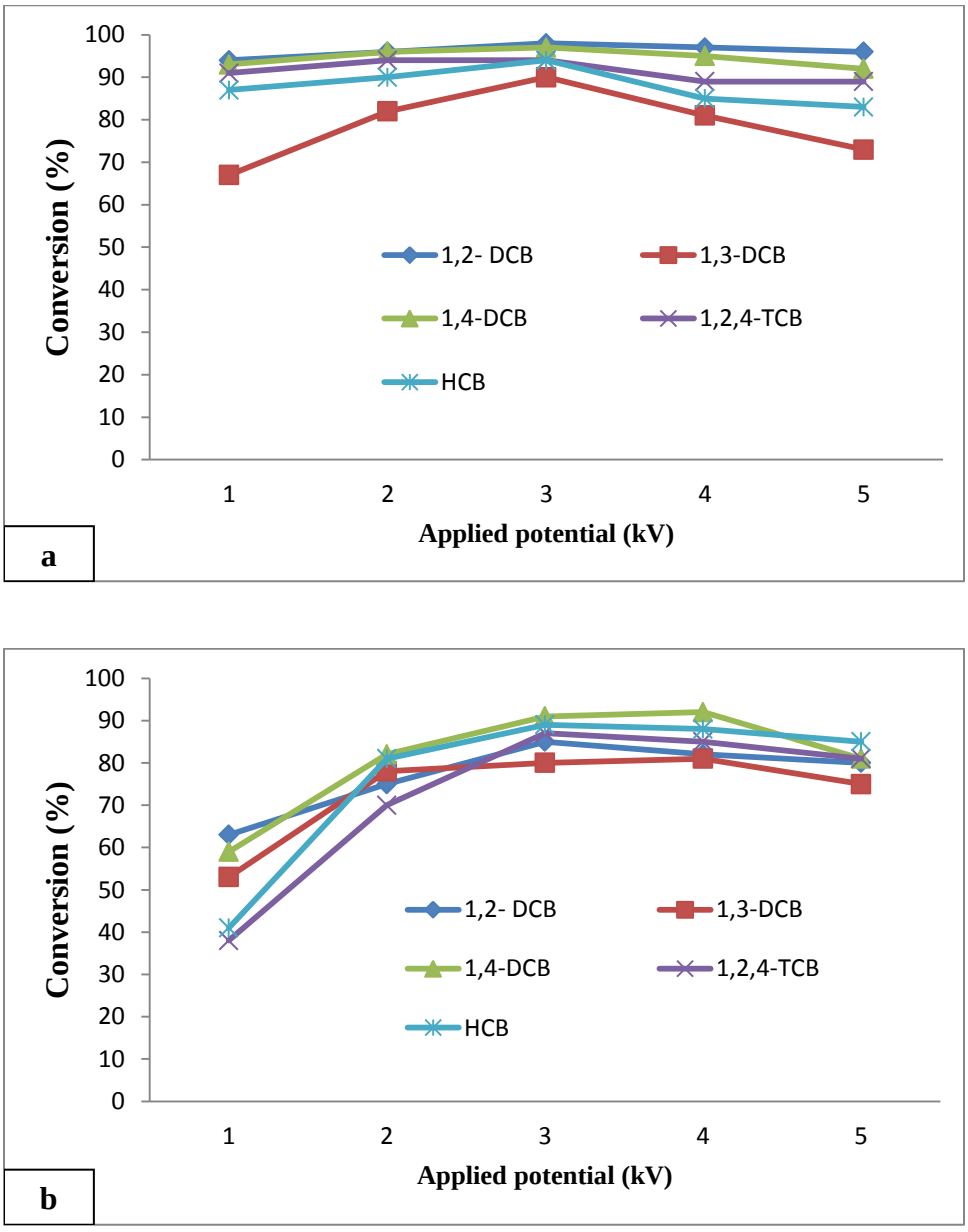


Figure 4-13 Effect of different applied potentials on the conversion ratio of chlorobenzenes (CBs) in the capillary-microreactor (at reaction time 20min and pH 10 by using (a) RHA-Pt and (b) RHA-Ti

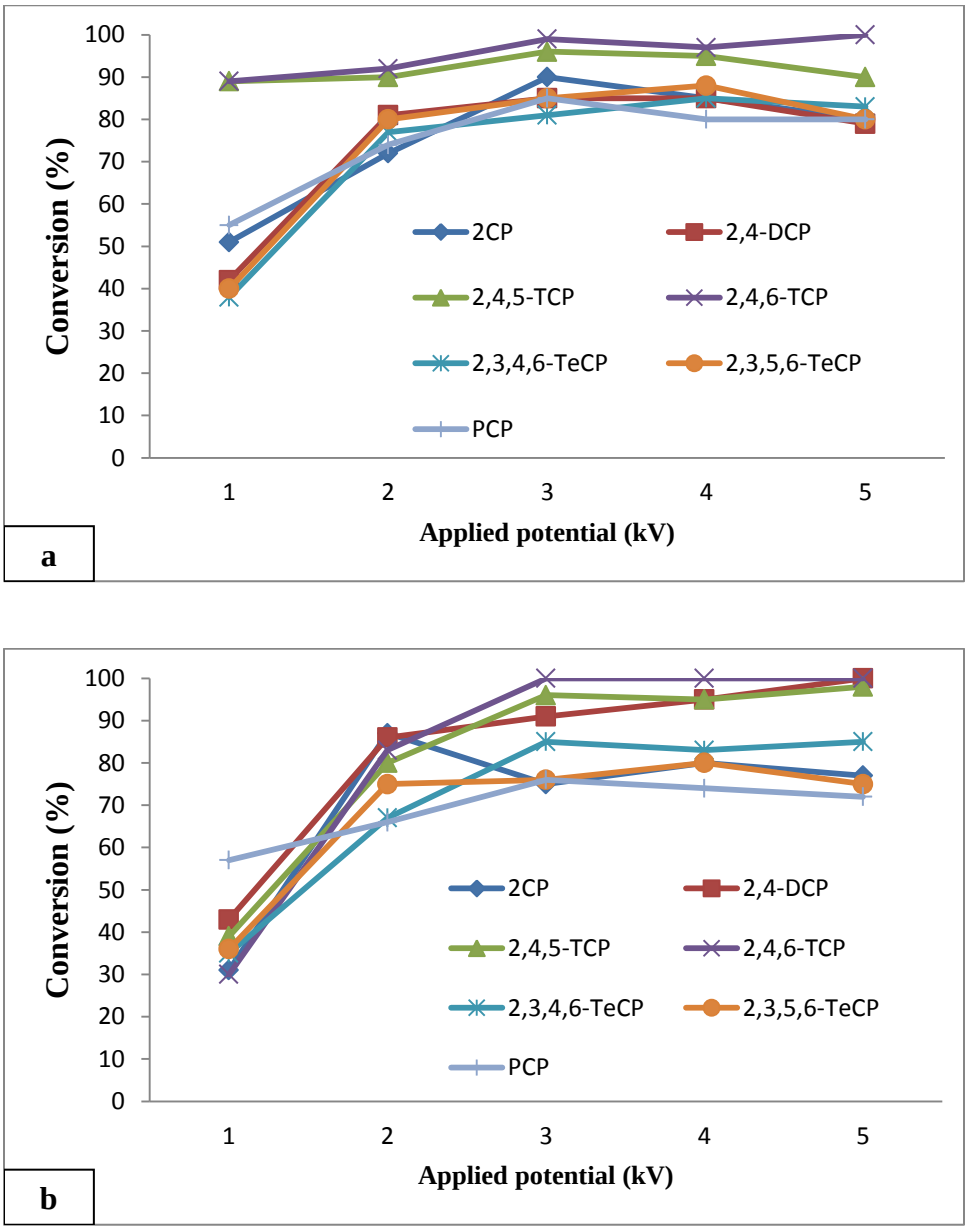


Figure 4-14 Effect of different applied potentials on the conversion ratio of Chlorophenols (CPs) in the capillary-microreactor (at reaction time 20min and pH 10 by using (a) RHA-Pt and (b) RHA-Ti

4.2.3 Effect of Reaction time

Reaction time is one of the most important factor in the HDC reactions. So, various reaction time (10 min, 20 min and 30 min) were applied. The reaction time was controlled manually; the conversion (%) of CBs and CPs with respect to these times is shown in Table 6 and Figures 15 and 16. The dechlorination increases with increase in reaction time, up to 20 min, by using RHA-Pt catalyst as seen in Fig 15 a and 16 a, while the best time for the dechlorination of CBs and CPs by using RHA-Ti as catalyst was 10 min as shown in Fig 15 b and 16 b .

Table 4-6 Effect of different reaction times on the conversion ratio in the capillary-microreactor of 21cm Length by applied potential 3kV

Catalyst	RHA-Pt			RHA-Ti		
Compound name	10 min	20 min	30 min	10 min	20 min	30 min
1,2- DCB	80	98	94	100	85	80
1,3-DCB	73	90	86	91	80	75
1,4-DCB	72	97	85	93	91	86
1,2,4-TCB	78	94	88	93	87	86
HCB	64	94	90	89	89	85
2CP	67	90	87	92	75	80
2,4-DCP	69	85	85	90	91	94
2,4,5-TCP	70	96	90	97	96	98
2,4,6-TCP	69	99	89	100	100	88
2,3,4,6-TeCP	65	81	80	100	85	94
2,3,5,6-TeCP	68	85	83	100	76	78
PCP	72	85	86	100	76	85

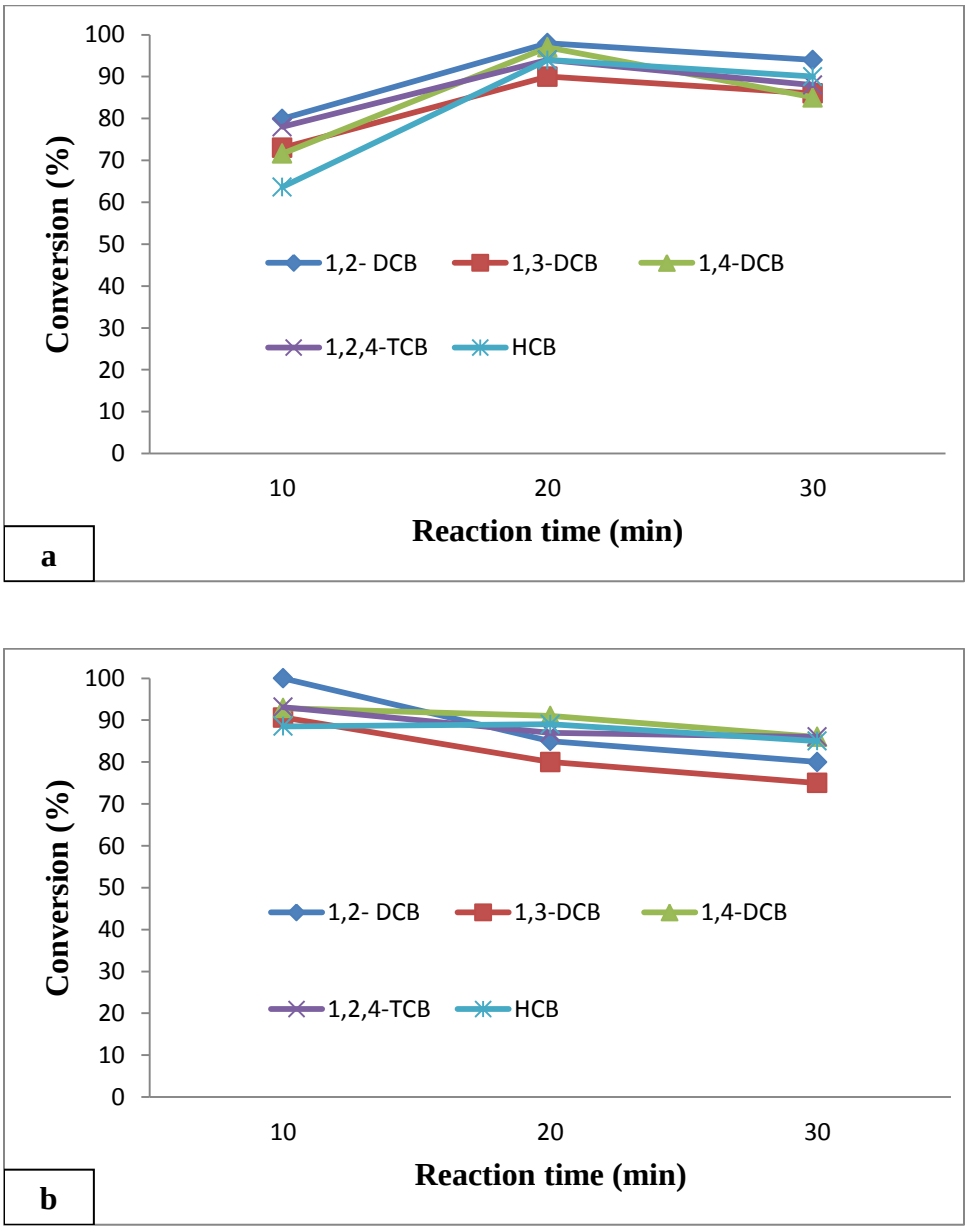


Figure 4-15 Effect of different reaction times on the conversion ratio of chlorobenzenes (CBs) in the capillary-microreactor of 21cm Length, applied potential 3kV (a) using pH 7 and RHA-Pt catalyst (b) using pH 10 and RHA-Ti catalyst

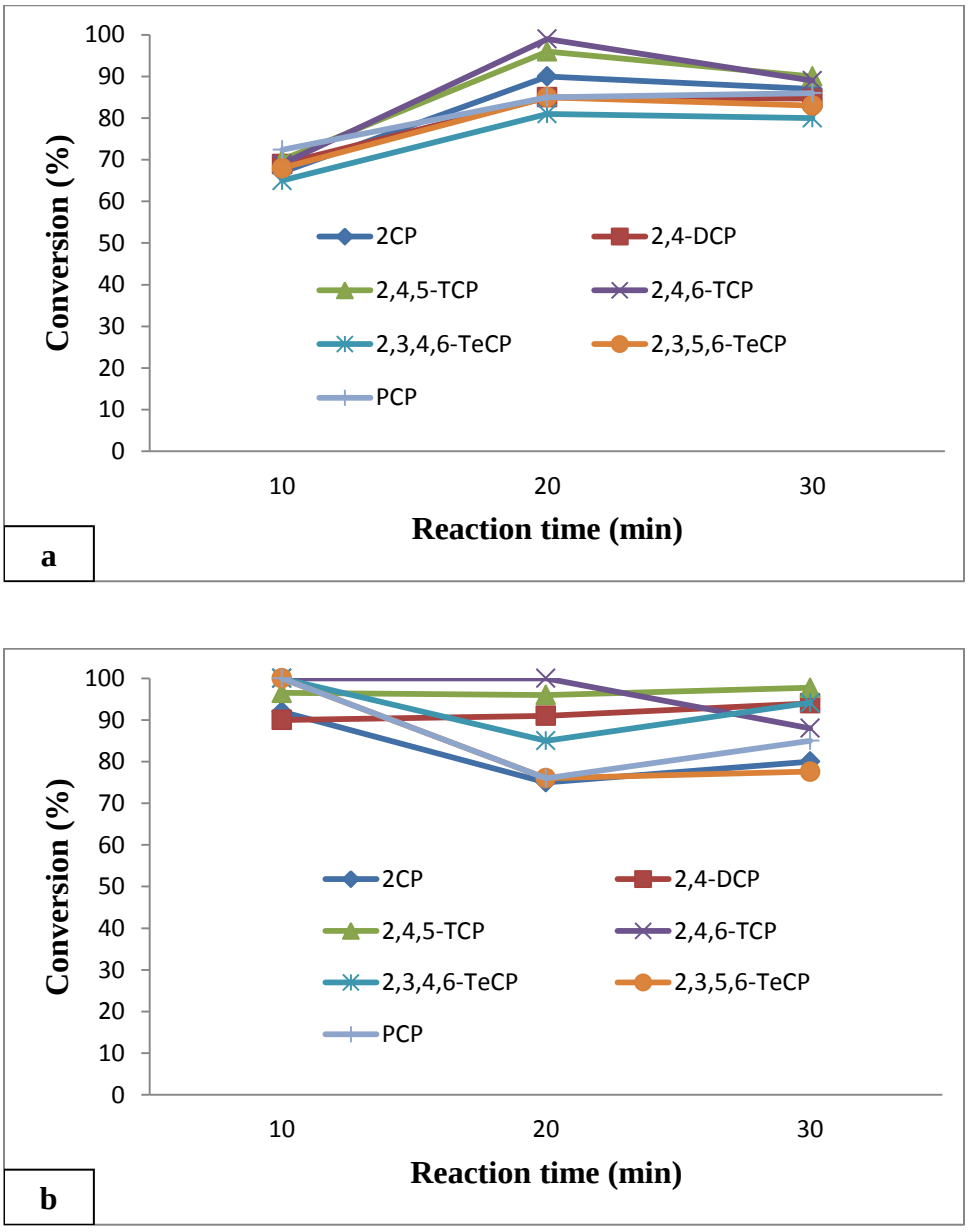


Figure 4-16 Effect of different reaction times on the conversion ratio of Chlorophenols (CPs) in the capillary-microreactor of 21cm Length, applied potential 3kV (a) using pH 7 and RHA-Pt catalyst (b) using pH 10 and RHA-Ti catalyst

4.2.4 Length of the capillary-microreactor

It has been reported that for microdevices using an electrophoretic separation at constant field, resolution is proportional to the square of the channel length. [40] Various lengths (7 cm, 14 cm, 21 cm) of the capillary were studied and significant improvement was obtained in the dechlorination of CBs and CPs when the length of the capillary was increased from 7cm to 21 cm shown in Figures 17,18 and Table 7.

Table 4-7 Effect of Length of the capillary microreactor on the conversion ratio of CBs and CPs

Compound name	Length of the capillary-microreactor		
	7 cm	14 cm	21 cm
1,2- DCB	92	95	98
1,3-DCB	87	89	90
1,4-DCB	94	95	97
1,2,4-TCB	89	91	94
HCB	90	92	94
2CP	72	81	90
2,4-DCP	82	84	85
2,4,5-TCP	81	88	96
2,4,6-TCP	97	98	99
2,3,4,6-TeCP	59	70	81
2,3,5,6-TeCP	65	78	90
PCP	50	68	85

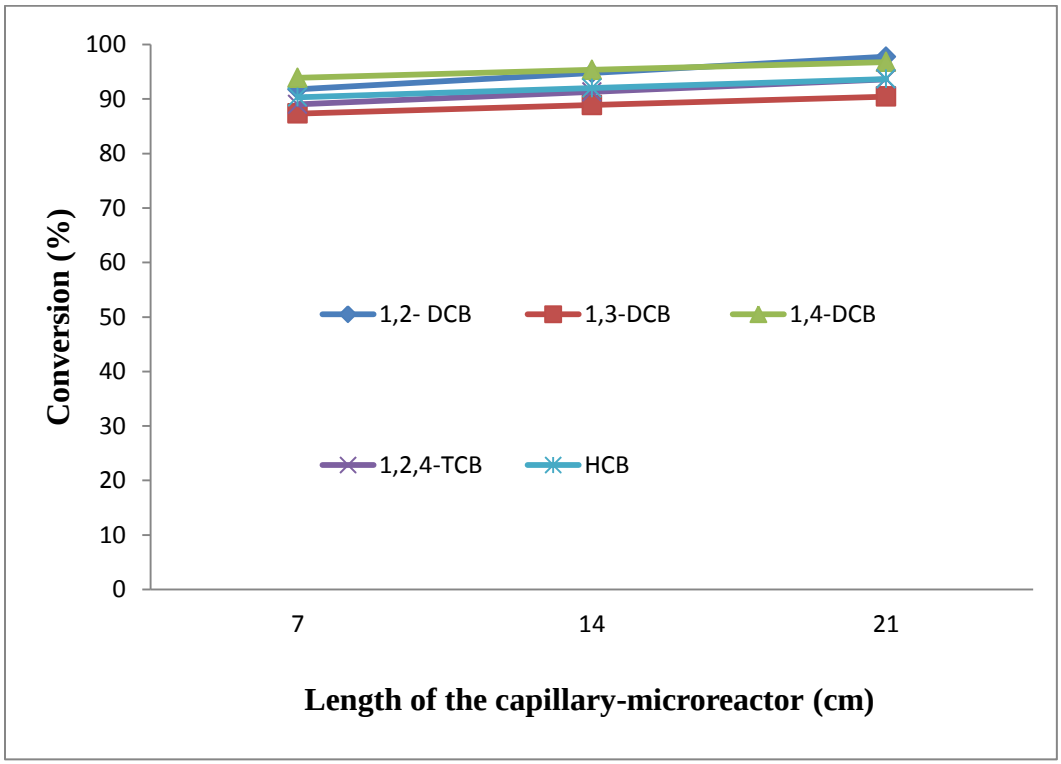


Figure 4-17 Effect of Length of the capillary microreactor on the conversion ratio of CBs and

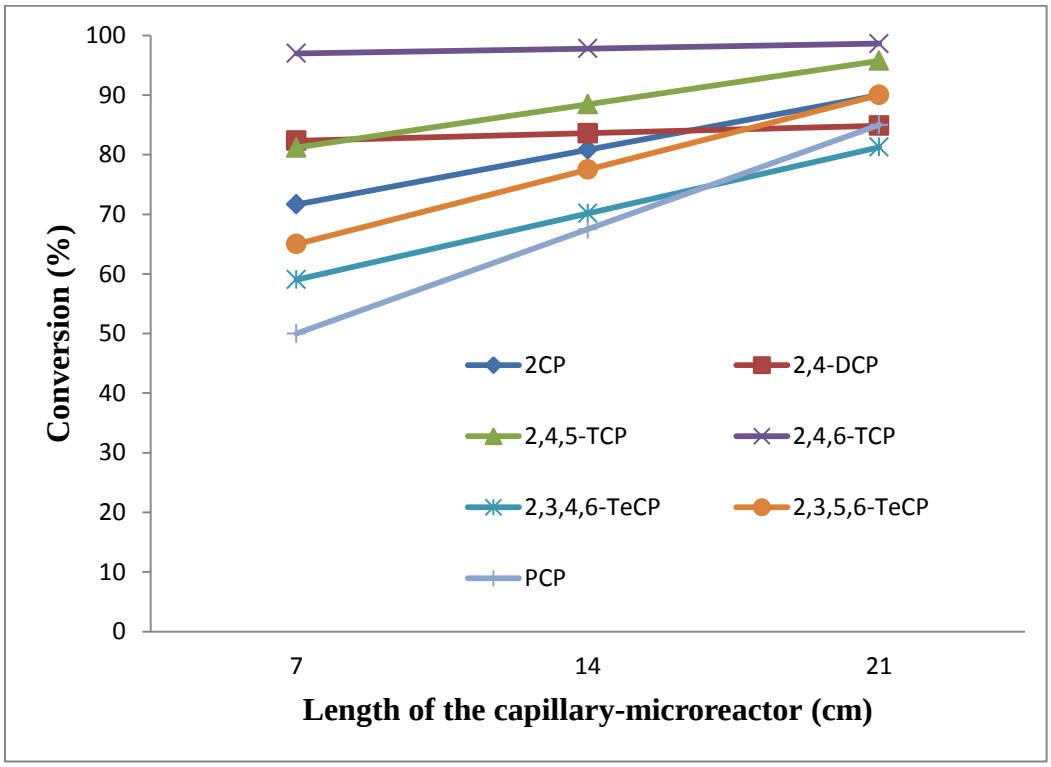


Figure 4-18 Effect of Length of the capillary microreactor on the conversion ratio of CPs

4.2.5 Reaction pH

The pH of the solution is an important parameter which controls the rate of the dechlorination of CBs and CPs in the capillary-microreactor. The pH of the solution studied was (2.0, 7.0 and 10). Table 8 summarizes the conversions of CBs and CPs by catalytic HDC in the capillary-microreactor using different buffer solutions to neutralize the HCl formed during the HDC reaction that reported as less aggressive medium. Figures (19,20) show the conversion of COCs involving different catalysts, the maximum conversion by using RHA-Pt catalyst was observed in neutral range (pH 7) compare to other buffer solutions this might be due to the dissolve of platinum particles.[28] while when RHA-Ti was used as catalyst the maximum conversion was obtained in alkaline range (pH 10).

Table 4-8 Effect of reaction pH on the conversion ratio of COCs in the capillary-microreactor (at 20min and applied potential 3kV)

Catalyst	RHA-Pt			RHA-Ti		
Compound name	pH 2	pH 7	pH 10	pH 2	pH 7	pH 10
1,2-DCB	96	100	98	81	83	86
1,3-DCB	92	96	90	78	76	80
1,4-DCB	94	98	97	79	88	91
1,2,4-TCB	100	97	94	87	83	88
HCB	90	91	94	65	72	89
2CP	72	81	71	74	76	75
2,4-DCP	82	95	85	87	87	91
2,4,5-TCP	97	96	96	90	94	96
2,4,6-TCP	97	97	92	92	84	100
2,3,4,6-TeCP	90	94	81	92	87	85
2,3,5,6-TeCP	94	90	78	88	79	83
PCP	85	79	74	76	80	88

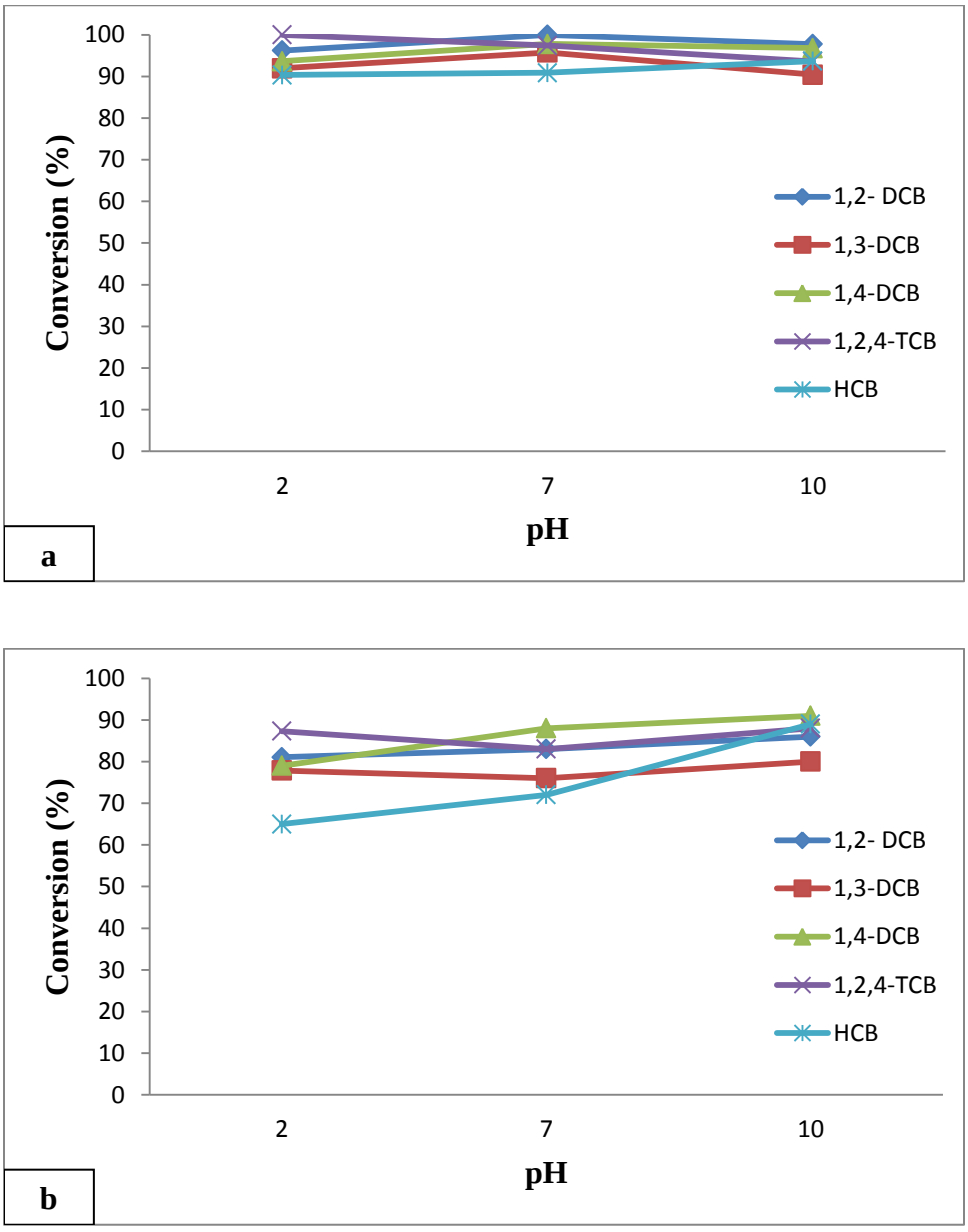


Figure 4-19 Effect of reaction pH on the conversion ratio of chlorobenzenes (CBs) in the capillary-microreactor (at 20min and applied potential (3kV) by using (a) RHA-Pt and (b) RHA-Ti

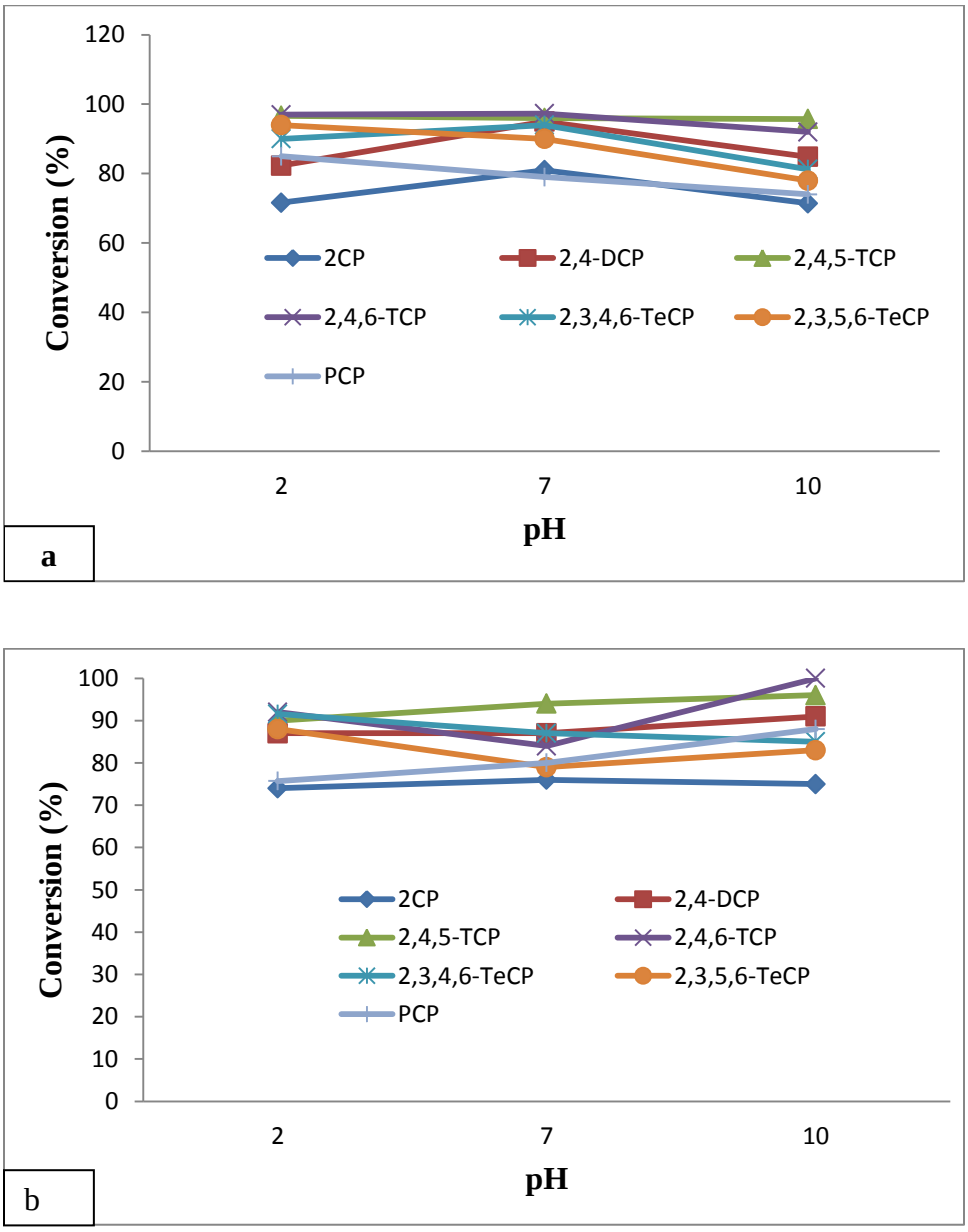


Figure 4-20 Effect of reaction pH on the conversion ratio of Chlorophenols (CPs) in the capillary-microreactor (at 20min and applied potential (3kV) by using (a) RHA-Pt and (b) RHA-Ti

4.2.6 Quantitative determination of Detoxification of COCs using the microreactor with (GC-MS)

In order to evaluate the most favorable reaction conditions,, the optimum dechlorination conditions reaction time of 20 min, and pH 7 by using RHA-Pt as the catalyst and 10 min applied potential of (3kV) was used with a 21 cm long capillary-microreactor, and pH 7 when the catalyst was RHA-Ti, Representative results are summarized in Table 9. Compared with conventional detoxification method, the capillary-microreactor provided high Conversion ratio of CBs and CPs in short time (10 min and 20 min) using little amount of the reactant, while the application of conventional method require long hours and higher amount of the reactant. Figure 21 shows GC-MS chromatogram of CBs and CPs before and after the detoxification of COCs in a glass capillary-microreactor in comparison with conventional method .while Figures 422 and 23 show GC-MS chromatogram of CBs and CPs before and after the detoxification of COCs by using the conventional method and in the glass capillary-microreactor respectively. Table 10 shows the compound name, retention time and peak number of target compounds in the GC-MS chromatogram

Table 4-9 Conversion ratio of CBs and CPs by the capillary-microreactor and the conventional method

Method	Glass capillary-microreactor		conventional method					
Catalyst	RHA-Ti	RHA-Pt	RHA-Pt			RHA-Ti		
Compound name	10 min	20 min	2HR	16HR	24HR	2HR	16HR	24HR
1,2-DCB	100	98	38	95	99	56	97	97
1,3-DCB	91	90	29	92	96	52	91	95
1,4-DCB	93	97	35	93	97	50	95	100
1,2,4-TCB	93	94	28	90	96	48	100	99
HCB	89	94	25	87	92	42	88	95
2CP	92	90	32	84	94	57	88	88
2,4-DCP	90	85	31	68	100	48	85	100
2,4,5-TCP	97	96	25	82	100	45	95	93
2,4,6-TCP	100	99	27	86	96	42	100	93
2,3,4,6-TeCP	100	81	22	79	97	44	100	100
2,3,5,6-TeCP	100	85	20	90	95	50	100	100
PCP	100	85	20	74	100	40	80	85

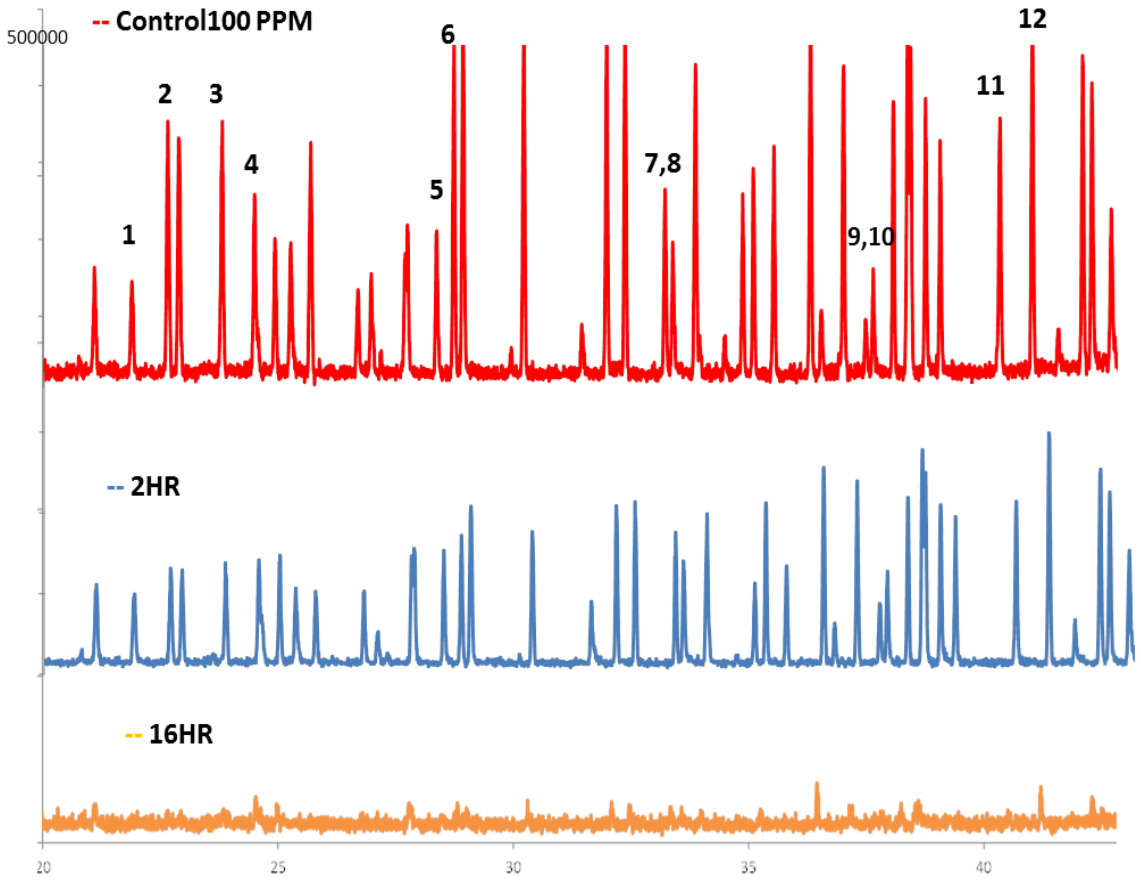


Figure 4-21 GC-MS chromatogram of CBs and CPs using conventional method , the control 100 ppm before a reaction occurs (Top), after 2 HR (middle) and after 16 HR (bottom). Peaks: 1 (2-chloroPhenol), 2 (1,4-dichlorobenzene), 3 (1,2-dichlorobenzene), 4 (1,3-dichlorobenzene), 5 (2,4-dichloroPhenol), 6 (1,2,4-trichlorobenzene), 7 (2,4,6-trichlorophenol), 8 (2,4,5-trichlorophenol), 9 (2,3,4,6-trichlorophenol), 10 (2,3,5,6-trichlorophenol), 11 (hexachloropenzene), 12 (pentachlorophenol)

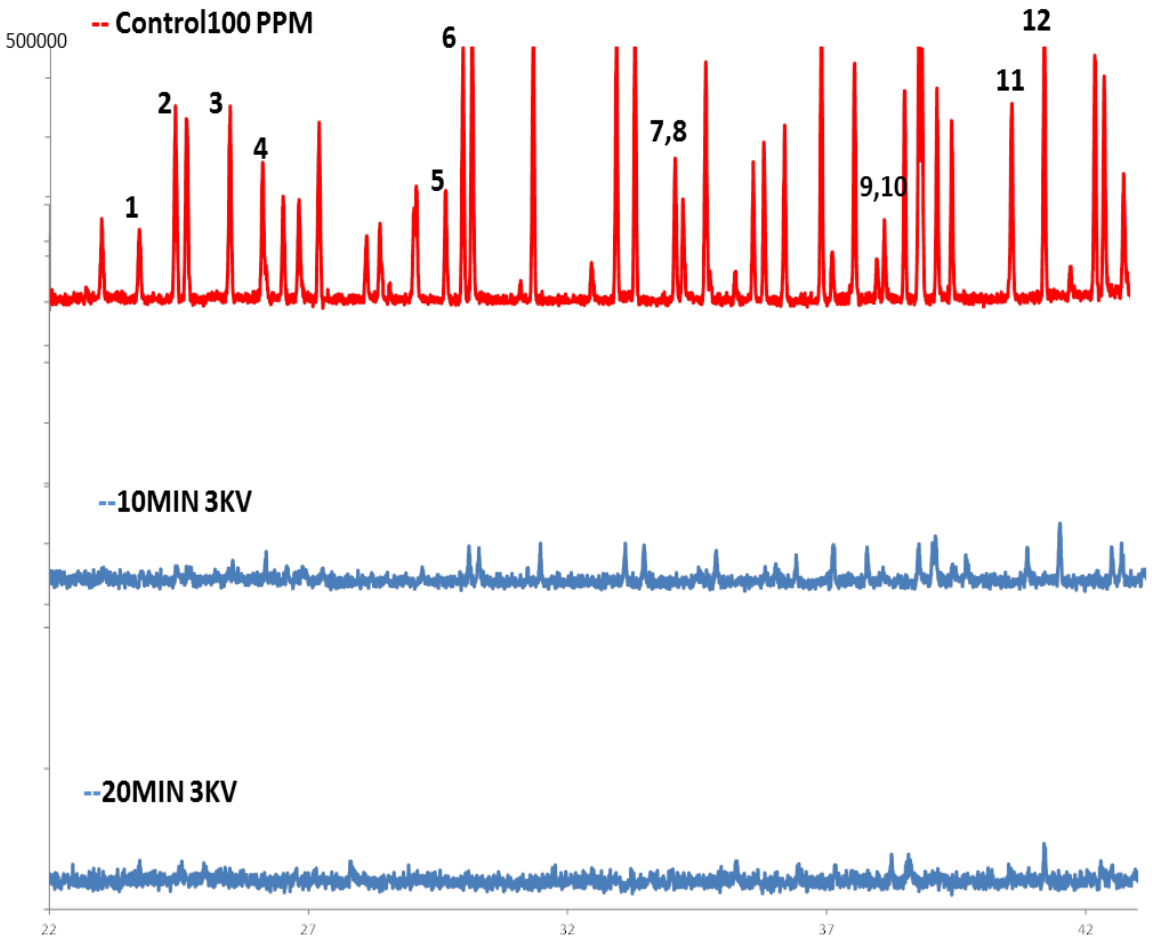


Figure 4-22 GC-MS chromatogram of CBs and CPs using the glass capillary-microreactor, the control 100ppm before a reaction occurs (Top), after 10min (middle) and after 20min (Bottom).). Peaks: 1 (2-chloroPhenol), 2 (1,4-dichlorobenzene), 3 (1,2-dichlorobenzene), 4 (1,3-dichlorobenzene), 5 (2,4-dichloroPhenol), 6 (1,2,4-trichlorobenzene), 7 (2,4,6-trichlorophenol), 8 (2,4,5-trichlorophenol), 9 (2,3,4,6-trichlorophenol), 10 (2,3,5,6-trichlorophenol), 11 (hexachloropenzene), 12 (pentachlorophenol)

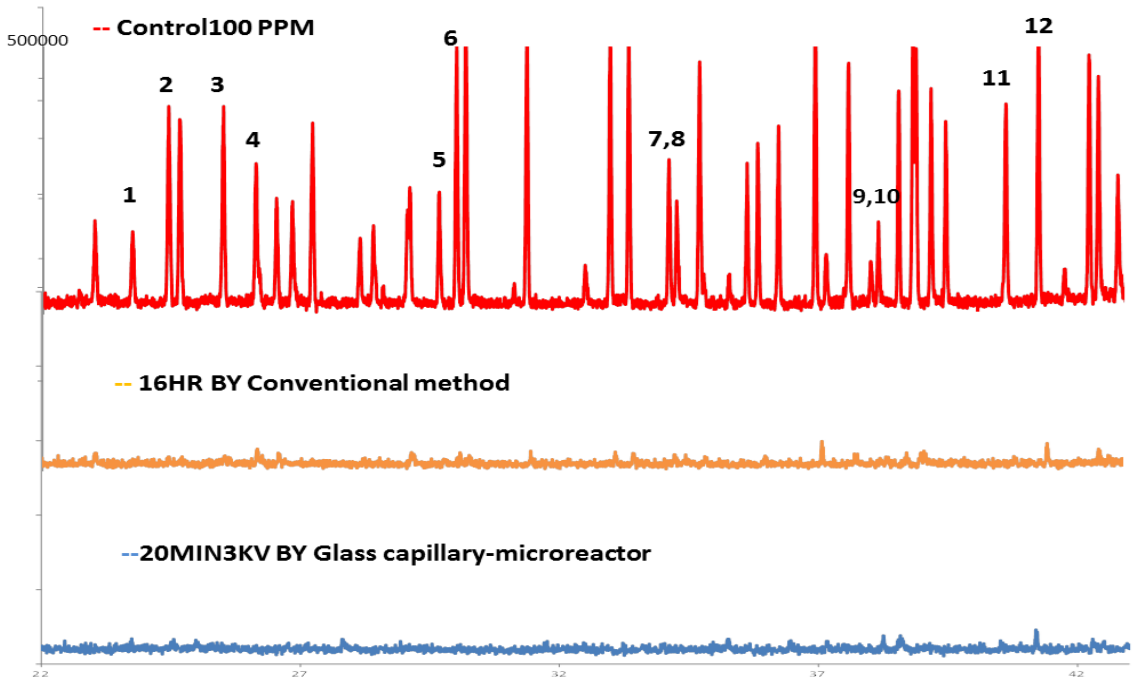


Figure 4-23 GC-MS chromatogram of CBs and CPs, the control 100ppm (Top), a glass capillary-microreactor after 20min (Bottom) in comparison with conventional method after 16HR (middle)). Peaks: 1 (2-chloroPhenol), 2 (1,4-dichlorobenzene), 3 (1,2-dichlorobenzene), 4 (1,3-dichlorobenzene), 5 (2,4-dichloroPhenol), 6 (1,2,4-trichlorobenzene), 7 (2,4,6-trichlorophenol), 8 (2,4,5-trichlorophenol), 9 (2,3,4,6-trichlorophenol), 10 (2,3,5,6-trichlorophenol), 11 (hexachloropenzene), 12 (pentachlorophenol)

Table 4-10 Compound name, retention time and peak number of target compounds in the GC-MS chromatogram

Compound Name	Retention Time	Peak Number
1,2-Dichloro-Benzene	23.824	3
1,3-Dichloro-Benzene	24.417	4
1,4-Dichloro-Benzene	22.682	2
1,2,4-Trichloro-Benzene	28.8	6
Hexachloro-Benzene	41.2	11
2-chloro-Phenol	21.907	1
2,4-Dichloro-Phenol	28.434	5
2,4,6-Trichloro-Phenol	33.338	7
2,4,5-Trichloro-Phenol	33.498	8
2,3,4,6-Tetrachloro-Phenol	37.635	9
2,3,5,6-Tetrachloro-Phenol	37.803	10
Pentachloro-Phenol	41.732	12

4.3 Mechanism of the dechlorination of CBs and CPs

In a glass capillary microreactor high potential (in Kv range) was applied to create in-situ generation of hydrogen as well as to expedite the activation of catalysts in the reaction for the detoxification of chlorobenzene and Chlorophenols. Moreover, the higher applied potential increases the analyte interaction with the nanoparticles and enhances the hydrodechlorination (HDC) reaction to detoxify of chlorobenzene and Chlorophenols [40,41]. In our reactor, we believe that the electron density on the surface of the catalysts and the hydrodechlorination HDC reaction increase by the applied potential .and thereby enhance conversion and the yield of benzene. Dechlorination proceeds in a stepwise manner to produce less or non chlorinated products as seen in Fig 27and 28 that show the proposed degradation pathway of CBs and CPs over RHA-Ti and RHA-Pt by using capillary-microreactor.

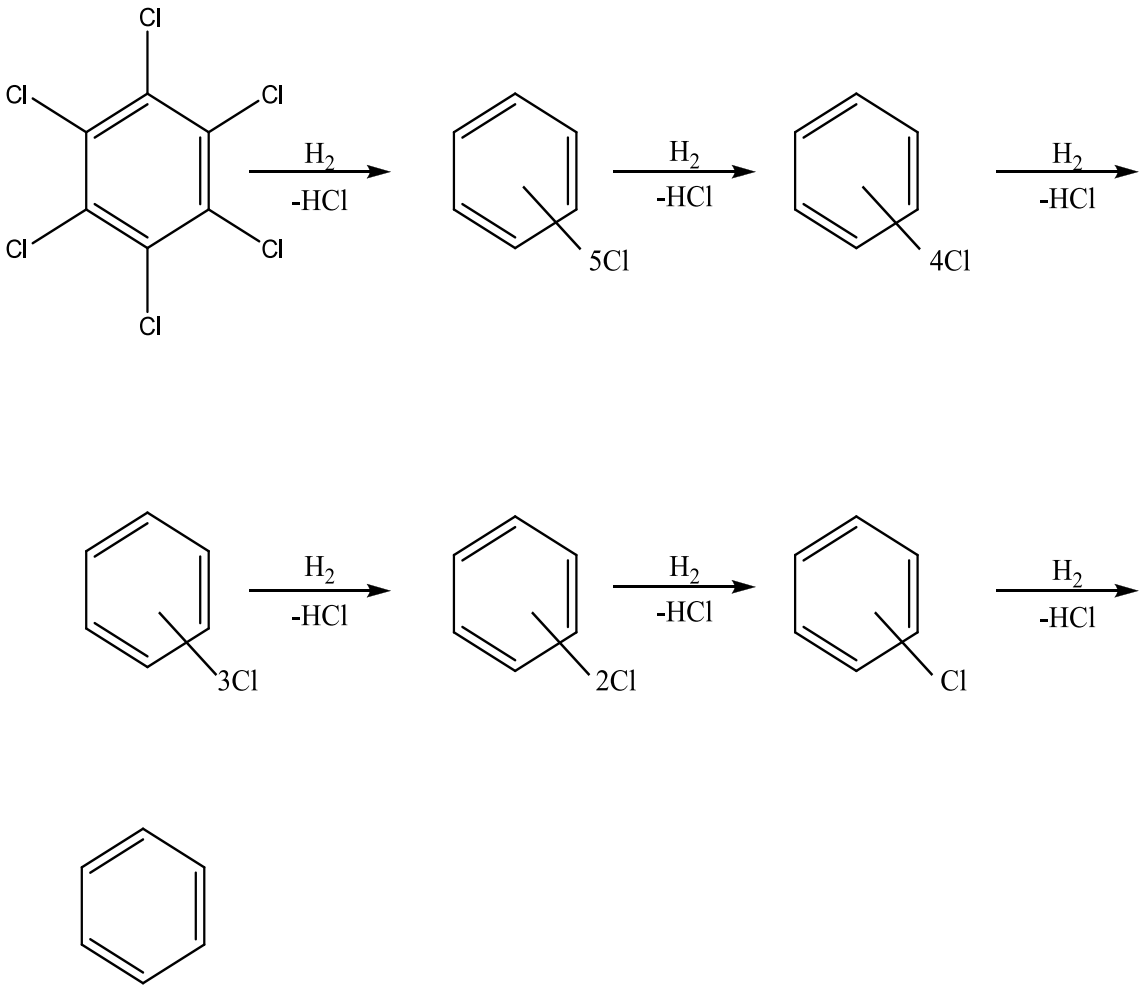


Figure 4-24 The proposed degradation pathway of CBs with RHA-Ti and RHA-Pt by using capillary-microreactor

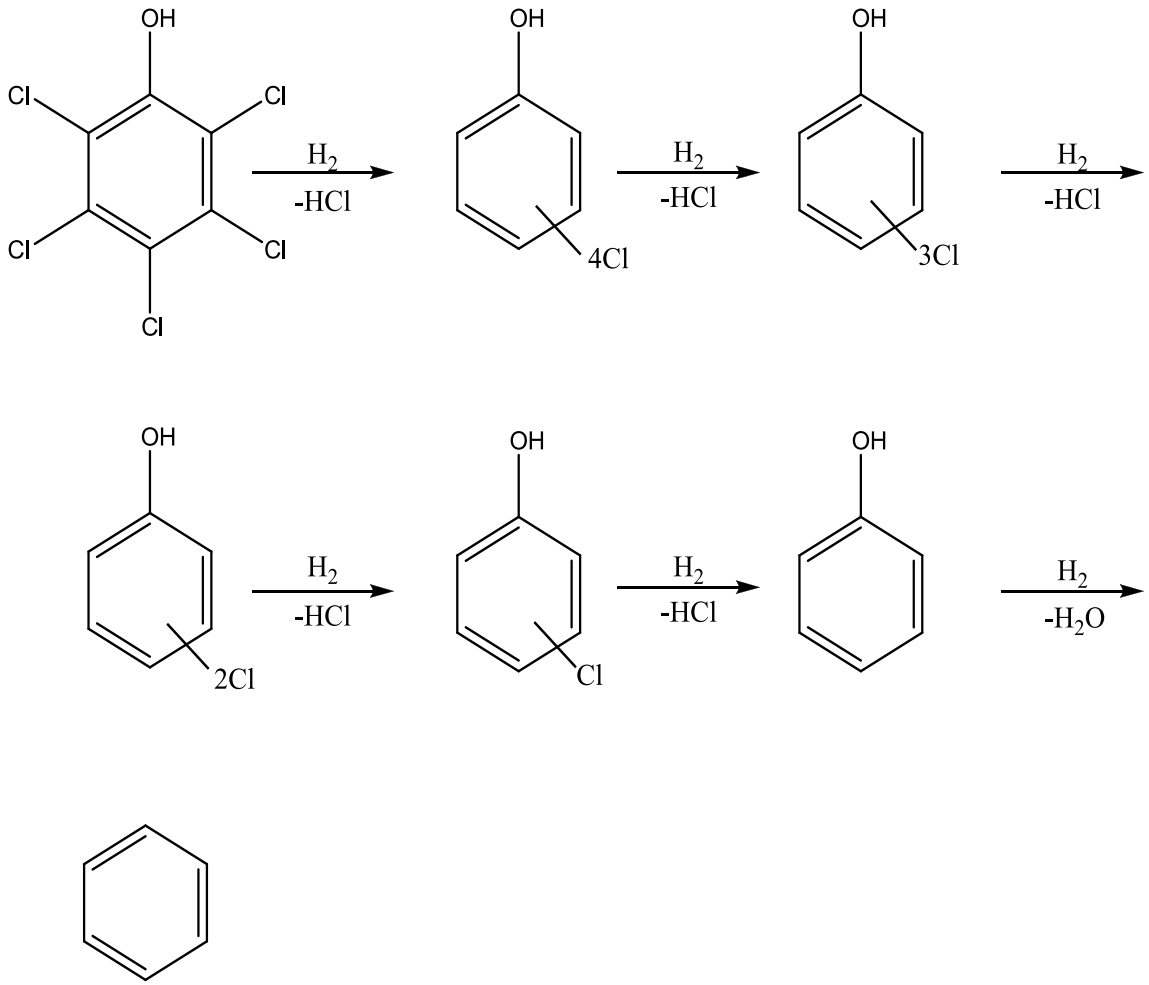


Figure 4-25 The proposed degradation pathway of Cps with RHA-Ti and RHA-Pt by using capillary-microreacto

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 CONCLUSION

We have demonstrated the detoxification of chlorobenzenes and chlorophenols (CBs and CPs) using a glass capillary-microreactor and conventinal hydrogention method. Experimnetal conditons were optimized to achieve better reaction performance. The buffer solutions used in the capillary reactor proved the medium for electrokinetic migration of target analytes. In this work, for the first time rice husk supported platinum (RHA-Pt) and Titanium (RHA-Ti) catalysts were used to investigate the detoxification of chlorobenzenes and Chlorophenols in a glass capillary microreactor. Our RHA-Ti and RHA-Pt. supported catalysts show very interesting catalytic activity in the HDC of CBs and CPs that were hydride chlorinated with yields of benzene under mild condition at room temperature and ambient pressure by using buffered solution. High potential (in Kv range) was applied to enhance the catalytic activity via electrokinetic mobility of the target analytes, no physical pumps are requied. The main advantage of this capillary reactor is in-situ generation of hydrogen for the detoxification of chlorobenzene and Chlorophenols. Only 20 min is sufficient to complete detoxify chlorobenzenes and Chlorophenols in capillary microreactor to compare with 24 HR reaction time in conventional catalytic method. The proposed method is simple, easy to use and suitable

for the detoxification of wide range of chlorinated organic pollutants. The method is environmentally benign and suitable for water decontamination applciations.

5.2 RECOMMENDATIONS

A few recommendations will be made to improve our method and catalysts properties and. Future work on these method and catalysts may include the following recommendations:

Recommendation1: More study is required to understad the mechanism of detoxification process in capillary microreactor.

Recommendation 2: We also recommend to investigate the selectivity and stability of synthesized catalysts for hydrodechlorination

Recommendation 3: Flow micro reactor could be used for scale up the reaction

References

[1] F. Vincent, F. Pierre, C. De Bellefon, S. Daniel, Ind. Eng. Chem. Res. 1999, 38, 4213.

[2] F. D. Kopinke, K. Mackenzie, R. Koehler, A. Georgi, J. Applied Catalysis A: General, 2004, 271,119

[3] Environmental Protection Agency. National Pollutant Discharge Elimination System, Code of Federal Regulations, 40, Part 122; U.S. Government Printing Office: Washington, DC, 1988.

[4] W. J. Hayes and E. R. Laws, Handbook of Pesticide Toxicology, Academic Press, San Diego, 1991.

[5] Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services. Toxicologic profile for alpha-, beta, gamma- and delta-hexachlorocyclohenxane, August 2005

[6] EURO CHLOR, 1,2,4-Trichlorobenzene Risk Assessment for the Marine Environment OSPARCOM Region - North Sea, 2002

[7] G.N. Jovanovic, P.Z. Plazl, P. Sakrittichai, and K. Al-Khaldi, Ind. Eng. Chem. Res. 2005, 44, 5099

[8] Z.Sun, W.Xuefeng, X.Hu, K.Wang, H.Shen, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2012, 414, 314

[9] A. Gallego, V.Gemini, S. Rossi, M.S. FortunatoM, E. Planes, C.E. Go´mez, S.E. Korol, International Biodeterioration & Biodegradation, 2009, 63, 1073

[10] E.R. Ritter, J.W. Bozzelli, and Dean, A.M., J. Phys. Chem., 1990, 94, 2493.

[11] M. Kosusco, M.E. Mullins, K. Ramanathan, K. and T.N. Rogers, Environ. Prog. 1988, 7, 136

[12] M. Wirtz, J. Klucik, M. Rivera, J. Am. Chem. Soc. 2000, 122, 1047

[13] T. Yamase, Appl. Catal., A: Gen. 2000, 195, 99

[14] J.G. Lin, Y.S. Ma, J. Hazard. Material 1999, 66, 291

[15] W.W. Mohn, J.M. Tiedje, Microbiol. Rev. 1992, 56, 482

[16] Y. Yamamoto, S. Tagawa, Environ. Sci. Technol. 2001, 35,

[17] B.V. Chang, C.W. Chiang, S.Y. Yuan, Chemosphere, 1998, 36, 537

[18] C.M. Kao, C.T. Chai, J.K. Liu, T.Y. Yeh, K.F. Chen, S.C. Chen, Water Res., 2004, 38, 663

[19] D.S. Shen, X.W. Liu, H.J. Feng, J. Hazard. Mater. B, 2005, 119, 239

[20] S. Wang, B. Yang, T. Zhang, G Yu, S. Deng, J Huang, Ind. Eng. Chem. Res, 2010, 49, 4561

[21] N.C. Concibido, T. Okuda, Y. Nakano, W. Nishijima, M. Okada, Tetrahedron Letters, 46 ,2005,3613.

[22] E.N. Balko, E. Przybylski, F. Von Trentini, Appl. Catal. B, 1993, 2, 1.

[23] R.A.W. Johnstone, A.H. Wilby, I.D. Entwistle, Chem. Rev., 1985, 85, 129

[24] X. Liu, G. Lu, Y. Guo, Y. Guo, Y. Wang, X. Wang, Journal of Molecular Catalysis A: Chemical, 2006, 252, 176

[25] F.D. Kopinke, K. Mackenzie, R. Koehler, A. Georgi Applied Catalysis A: General, 2004, 271, 119.

[26] F.H. Ribeiro, C.A. Gerken, G. Rupprechter, G.A. Somorjai, C.S. Kellner, G.W. Coulston, L.E. Manzer and L. Abrams, J. Catal., 1998, 176, 352.

[27] C.D. Thompson, R.M. Rioux, N. Chem, and F.H. Ribeiro, J. Phys. Chem. B, 2000, 104, 3067.

[28] I.M. Nangoi, P. K. Kiyohara, L.M. Rossi, Applied Catalysis B: Environmental 2010, 100, 42.

[29] F.J. Urbano, J.M. Marinas, J. Mol. Catal. A: Chem. 2001, 173, 329.

[30] T. Naota, H. Takaya, S. Murahashi, Chem. Rev., 1998, 98, 2599

[31] Z.M. de Pedro, J. A. Casas, L. M. Gomez-Sainero, J. J. Rodriguez, Applied Catalysis B: Environmental, 2010, 98, 79

[32] S. Gryglewicz, W. Piechocki, Chemosphere, 2011, 83, 334.

[33] V. Calo`, A. Nacci b, A. Monopoli, A. Damascelli, E. Ieva, N. Cioffi, Journal of Organometallic Chemistry 2007, 692, 4397

[34] K. Mallick, M. Witcomb, M. Scurrell, Mater. Chem. Phys. 2006, 97, 283.

[35] H. Wang, J. Wang, Applied Catalysis B, Environmental, 2007

[36] M. Bron, M. Bonifer, A. Knop-Gericke, D. Teschner, J. Kröhnert, F.C. Jentoft, R. Schlögl, P. Claus, Towards the pressure and material gap in heterogeneous catalysis: hydrogenation of acrolein

[37] F. Adam, J. N. Appaturi, R. Thankappan, M. Asri, M.Nawi, Applied Surface Science , 2010, 257, 811

[38] J. Bedia, L.M. Gómez-Sainero, J.M. Grau, M. Busto, M. Martin-Martinez, J.J. Rodriguez, Journal of Catalysis, 2012, 294, 207.

[39] S. Tadepalli, R. Halder, A. Lawal, Chemical Engineering Science, 2007, 62, 2664

[40] C. Basheer, F. Shahitha, J. Hussain, HK Lee and S. Valiyaveettil, Tetrahedron Lett., 2004, 45, 7297.

[41] C. Basheer, S. Swaminathan, HK Lee, S. Valiyaveettil, Chem. Commun, 2005, 409.

[42] P. Chowdhury, T. Viraraghavan, Science of the Total Environment, 2009,407, 2475

[43] L. Calvo, M.A. Gilarranz, J.A. Casas, A.F. Mohedano, J.J. Rodr´ıguez, Journal of Hazardous Materials,2009, 161, 842

[44] UNEP, 2002 United Nations Environment Program (UNEP), 2002. Regional assessment of persistent toxic substances. South East Asia and South Pacific regional report. UNEP Chemicals, Switzerland

[45] M. Vidali, Pure Appl. Chem., 2001, 73, 1163.

[46] M. A. Aramendía, V. Boráu, I. M. García, C. Jiménez, F. Lafont, A. Marinas, JV. M. Marinas, F. J. Urbano, J. Mol. Catal. A: Chem, 2002184, 237.

[47] Y. Z. Chen, C. W. Liaw, L. I. Lee, Appl. Catal. A: Gen., 1999, 177, 1.

[48] S. H. Tabaei, C. U. Pittman, Tetrahedron Lett, 1993, 34, 3263.

[49] G. Yuan, M. A. Keane, J. Catal., 2004, 225, 510.

[50] S. Ordoñez, F.V. Díez, H. Sastre, Appl. Catal. B, 2000, 25, 49.

[51] V. I. Kovalchuk, J. L. d‟Itri, Appl. Catal. A: Gen., 2004, 271, 13.

[52] H. Li and P. E. Smith, J. Phys. Chem. B, 2003, 107, 1396

[53] S. Ordoñez, F.V. Díez, H. Sastre, Appl. Catal. B, 2001, 31, 113.

[54] S. Ordoñez, F.V. Díez, H. Sastre, Appl. Catal. B, 2003, 40, 119.

[55] E. López, S. Ordóñez, F.V. Díez, Appl. Catal. B, 2006, 62, 57.

[56] X. Liu, G. Lu, Y. Guo, Y. Guo, Y. Wang, X. Wang, Journal of Molecular Catalysis A: Chemical, 2006, 252, 176

[57] M,-T. Tsay, F.-W. Chang, Applied Catalysis A: General, 2000, 203, 15

[58] F. Adam, J. N. Appaturi, Z. Khanam, R. Thankappan, M. Asri, M. Nawi, Applied Surface Science, 2013, 264, 718

[59 F. Adam, J. N. Appaturi, A. Iqbal, Catalysis Today, 2012, 190 (2012)

[60] K. Jahnisch, V. Hessel, H. Lowe, M. Baerns, Angew. Chem. Int. Ed. 2004, 43, 406

[61] S. Tadepalli, R. Halder, A. Lawal, Chemical Engineering Science, 2007, 62 , 2663

[62] I.M. Nangoi, P. K. Kiyohara, L.M. Rossi, Applied Catalysis B: Environmental 2010, 100, 42.

Vitae

Name :Abdulelah Ahmed Ali Thabet

Nationality :Yemeni

Date of Birth :1/2/1980

Email :g200803760@kfupm.edu.sa , aast_124@yahoo.com

abdulelahthabet1@gmail.com

Address :Chemistry Department, Faculty of Education and Arts Khawlan, Sana'a University, Sana'a Yemen P. O. Box (1247)

Mobile : +966 505527795 (Saudi Arabia) +967771535795 (Yemen)

Academic Background :-M.Sc. in Chemistry Science, King Fahd University of Petroleum and Minerals (KFUPM), Dhahran, Saudi Arabia, 2013

-B.Sc. in Chemistry Science, Sana'a University, Sana'a, Yemen, 2002